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GUIDANCE DOCUMENT  
FOR THE CONTROL OF WATER POLLUTION  
IN THE PHOTOGRAPHIC PROCESSING INDUSTRY

CONTRACT NO. 68-01-3273, Task 11  
CONTRACT NO. 68-01-4826  
CONTRACT NO. 68-01-5767, Task 6 and Task 17

Prepared For:

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401 M Street, S.W.  
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Prepared By:

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Springfield, Virginia 22151

20 FEBRUARY 1981

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## SECTION I

### CONCLUSIONS

This guidance document is the result of a study of the photographic processing industry by the Effluent Guidelines Division of the Environmental Protection Agency. The purpose of the document is to assist local authorities and other interested parties in the control of wastewater pollutants from photographic processing facilities where required. The toxic pollutants of concern which may be present in the raw wastewater are silver, cyanide, and chromium. Silver is present in the raw waste in all facilities and cyanide is present in the raw wastewater in many color processing facilities. Chromium is present in only those facilities which use dichromate bleach. The use of this bleach is generally restricted to some processors of commercial movie film.

Conventional silver recovery (consisting of metallic replacement or electrolytic or both) and ferricyanide bleach regeneration are widely practiced as in-process controls by most of the industry because of economic benefits. Recovery of silver from wash water using ion exchange or reverse osmosis are advanced controls not widely used, although the use of ion exchange is increasing. The use of various in-process controls and treatments by the industry is estimated in Table I-1.

TABLE I-1  
ESTIMATED BREAKDOWN OF IN-PROCESS CONTROL AND TREATMENT USE  
BY PLANT SIZE (DAILY PRODUCTION)

PERCENTAGE OF PLANTS USING INDICATED CONTROLS BY SIZE CATEGORY						
Pro- duction sq m/ day	Conven- tional Silver Recovery	Ion Exchange	Reverse Osmosis	Ferri- cyanide Bleach Regen- eration	Ferrous Sulfate Precipi- tation	Di- chromate Treat- ment
<93	*	0	0	*	0	0
93-186	95	2	0	50	0	0
186-464	100	8	0	60	0.3	0
464-4,640	100	2	0	90	3	0
over 4,640	100	20	33	95	20	0

\* Insufficient information to make reasonable estimate.

These controls reduce the waste loads of silver and cyanide by up to 85 percent. It was also established that more than 99 percent of the photographic processing facilities are indirect dischargers to publicly owned treatment works (POTW) and less than one percent of the facilities have a direct discharge.

Based on the information presented in Section VII, it has been demonstrated that photographic processing facilities can achieve the effluent levels using the indicated in-process control and end-of-pipe treatment technologies described in this guidance document. To determine the 30-day average and single-day maximum silver values, the plant data mean was multiplied by the appropriate variability factors listed in Table VII-12. In the case of total cyanide, the computed single-day variability factor of 12 is inordinately high. A large number of cyanide values were reported which were at the detection limit of the analytical procedures used (0.005 mg/liter). This caused the distribution of data to be badly skewed and resulted in the high variability factor. For this reason the

variability factors for total cyanide were calculated using the individual plant data given in Table VII-4. The calculated total cyanide variability factors at a 99 percent confidence level are 3.7 for the single-day maximum and 1.2 for the 30-day average maximum (see Table VII-12).

Chromium is used in bleach formulations for one color print film and for black and white reversal motion picture films. No known plants in the photographic processing industry using these processes treat their wastewater for the specific reduction of total chromium, and therefore no chromium data from treated effluent were available. The total chromium variability factors determined for the metal finishing industry are used to determine the 30-day and single-day maximum limits. These factors are 1.43 and 4.94, respectively. The average total chromium concentration in the effluents from all plants studied in the metal finishing industry was 0.57 mg/liter after treatment consisting of chromium reduction, chemical precipitation, and clarification. The addition of filtration reduced the effluent chromium level to 0.32 mg/liter. The pollutant amounts were calculated using these concentrations and the average hydraulic load of 157,000 liters/1,000 sq m (3,850 gal/1,000 sq ft) for the photographic processing industry. It is recommended that the after dichromate bleach wash water and waste dichromate bleach be segregated and treated separately from other wastewaters. This reduces the volume of wastewater that must be treated and reduces potential interferences from other photoprocessing chemicals.

The following toxic pollutant levels are given in the form of amount of pollutant per unit of production. Concentration levels are also given for informational purposes. The Agency does not recommend the use of concentration based limitations for controlling pollutants at facilities in the industry. There is, as shown in Section VII, a poor relationship between concentration and the amount of pollutant discharged. The Agency encourages the reduction of wastewater quantities by various water saving controls. Concentration limitations for this industry tend to discourage water use reductions. The silver concentrations given below were calculated from the production normalized amounts and the average production normalized hydraulic load for the industry. For cyanide and chromium, the production normalizing factor is based on the

amount of material processed using ferricyanide or  
dichromate bleach, respectively.



## I. Silver Controls

### Conventional Silver Recovery

	<u>Variability Factor</u>	<u>Effluent Silver Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (from Table VII-6)		0.14 (0.029)	0.90
30-day average maximum	1.3	0.19 (0.038)	1.1
Single-day maximum	4.2	0.59 (0.12)	3.7

### Conventional Silver Recovery Plus Ion Exchange Treatment of Wash Waters

	<u>Variability Factor</u>	<u>Effluent Silver Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (from Table VII-8)		0.048 (0.0098)	0.31
30-day average maximum	1.3	0.062 (0.013)	0.40
Single-day maximum	4.2	0.20 (0.041)	1.31

Conventional Silver Recovery plus Reverse Osmosis Treatment of Wash Water and Precipitation of Silver from Concentrate

	<u>Variability Factor</u>	<u>Effluent Silver Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (from Table VII-8)		0.0088 (0.0018)	0.06
30-day average			
maximum	1.3	0.011 (0.0023)	0.07
Single-day			
maximum	4.2	0.037 (0.0076)	0.24

## II. Cyanide Controls

### Ozone Regeneration of Ferricyanide Bleach

	<u>Variability Factor</u>	<u>Effluent Total Cyanide Amount, kg/1,000 sq m (lb/1,000 sq ft)*</u>	<u>Concentration Range,** mg/liter</u>
Plant data mean (from Table VII-3)		4.8 (0.98)	0.4-1.4
30-day average			
maximum	1.2	7.3 (1.2)	
Single-day			
maximum	3.7	24 (3.6)	

### Ozone Regeneration of Ferricyanide Bleach plus Ferrous Sulfate Precipitation Treatment on Waste Fix

	<u>Variability Factor</u>	<u>Effluent Total Cyanide Amount, kg/1,000 sq m (lb/1,000 sq ft)*</u>	<u>Concentration Range,*** mg/liter</u>
Plant data mean (from Table VII-4)		1.1 (0.23)	0.7-10
30-day average			
maximum	1.2	1.7 (0.28)	
Single-day			
maximum	3.7	5.9 (0.85)	

\* Based on amount of material processed with ferricyanide bleach.

\*\* The plants exhibiting this concentration range have a ferricyanide bleach production range of 0.3 to 15 percent of the total production.

\*\*\* The plants exhibiting this concentration range have a ferricyanide bleach production range of 4 to 100 percent of the total production.

NOTE: The cyanide concentration in the effluents from plants using ferricyanide bleach may exhibit wide variations related to the ratio of ferricyanide production to the total production.

### III. Chromium Controls

#### Chromium Reduction, Precipitation, and Clarification Treatment of Dichromate Bleach Wastes

	<u>Variability Factor</u>	<u>Effluent Total Chromium Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (see text)		0.088 (0.018)	0.57
30-day average maximum	1.43	0.13 (0.026)	0.82
Single-day maximum	4.94	0.43 (0.089)	2.8

#### Chromium Reduction, Precipitation, Clarification, and Filtration Treatment of Dichromate Bleach Wastes

	<u>Variability Factor</u>	<u>Effluent Total Chromium Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (see text)		0.049 (0.010)	0.32
30-day average maximum	1.43	0.070 (0.014)	0.46
Single-day maximum	4.94	0.24 (0.049)	1.6

## SECTION II

### SUMMARY

The photographic processing industry consists of facilities which process various silver halide sensitized photographic products for external customers. There are approximately 11,000 processing facilities distributed throughout the United States. More than 99 percent of the facilities discharge wastewater to POTW's; less than 20 plants were found that discharge directly to surface waters. The industry is divided into four groups: portrait studios (SIC 7221), commercial studios (SIC 7333), photofinishers (SIC 7395), and movie film processors (SIC 7819). The majority of facilities (about 9,900) process less than 93 sq m (1,000 sq ft) of product per day and account for about 12 percent of the total U.S. production. The emphasis of information gathering during this study was directed to plants with production greater than 93 sq m per day which, as a group, accounts for 1,100 plants and 88 percent of the U.S. production.

Photographic processing consists of treating a silver halide sensitized material with a series of chemical solutions and wash water steps to produce a visible image in black and white or color. There are more than 20 different processes used with variations in the solution chemistry and the sequence of solution treatment. Most facilities process a variety of materials and use more than one process. There was no strong basis for subcategorization of the industry based on process use or any of the other factors considered.

The major sources of process wastewater are from waste chemical solutions and waste wash waters. The toxic pollutants found in significant amounts in the plant raw wastewater are silver, cyanide, and chromium. The silver is contained in the emulsion of all the processed materials and is present in the wastewaters from all facilities. Cyanide and chromium are present in some bleach solutions in the form of ferri-ferrocyanide and dichromate compounds, respectively, and are present in the wastewaters from only those facilities which use these types of bleach. It is recognized that silver and cyanide in wastewaters from

photoprocessing facilities are not in a free ionic state but, rather, the silver is combined with thiosulfate as a silver thiosulfate complex and the cyanide is combined with iron as an iron cyanide complex (ferri-ferrocyanide). Cadmium may also be present in the wastewaters in some facilities. It is present in the emulsion of some photographic materials and appears in the wastewaters of facilities which process these materials. Industry has stated that an effort is being made to eliminate cadmium as a constituent of these materials.

The industry removes up to 85 percent of the silver and cyanide, using conventional in-process controls which recover the silver from waste-fix solutions and regenerate ferricyanide bleach for reuse. Other in-process controls in use include ferric EDTA bleach regeneration and process tank squeegees which result in general waste load reductions. These in-process controls are almost universally used throughout the industry and are primarily for the economic benefit gained from silver recovery and chemical savings.

Advanced in-process controls, consisting of ion exchange or reverse osmosis, countercurrent washing, and wash water recycle, are used by some plants. Ion exchange or reverse osmosis is used for recovery of silver from after-fix wash water which contains approximately 10 percent of the totally available silver. Countercurrent washing and wash water recycle (after ion exchange or reverse osmosis) reduce the overall plant hydraulic load. Although there may be some additional economic benefit from using these advanced controls, the usual purposes are conservation and the environmental benefit. The use of these in-process controls in conjunction with standard silver recovery and ferricyanide regeneration reduces silver and cyanide loads by up to an additional nine percent. Controls involving the recycle or reuse of recovered chemicals are not universally applicable to all processes, products, or plant configurations because of the potential effect on product quality. Ion exchange and reverse osmosis treatment of wash waters represent complex advanced technology and requires careful design, selection and installation of equipment, close operating attention, and proper maintenance to achieve reliable results. These requirements could limit potential applications of this technology.

End-of-pipe wastewater treatments are not widely used in the photographic processing industry. Some plants treat waste fix after silver recovery with ferrous sulfate precipitation and settling to reduce the ferricyanide load prior to discharge. Other treatments such as equalization, neutralization, aeration, ozonation, and filtration are used at some plants for waste load reduction to meet specific locally imposed effluent quality requirements.

The use of dichromate bleach is generally limited to facilities which process movie film and only those facilities will have chromium in their wastewater effluent. There are no known facilities in the photographic processing industry which regenerate dichromate bleach or treat their wastewater to reduce the amount of chromium discharged. One facility uses a replenishment-on-demand system to limit the amount of dichromate bleach used to the minimum amount required by the process. The metal finishing industry has demonstrated that a treatment system, consisting of hexavalent chromium reduction, pH adjustment for chromium precipitation, and filtration, is effective in reducing the amount of chromium discharged.

One photographic processing plant has installed an extensive in-process control and end-of-pipe treatment system to approach zero wastewater discharge. The system includes advanced solution reuse, wash water recycle, countercurrent washes, reverse osmosis, ion exchange, and multi-stage evaporation. The applicability of this system to the entire photographic processing industry appears to be limited. The plant using the system is a very large portrait studio which can control the number and type of products and processes used. The system may not be practical for small and medium plants for economic reasons and for plants with more complex product mixes for technical reasons.

This study included the gathering of information related to the cost of installing and operating the various in-process controls and end-of-pipe treatment technologies. Conventional silver recovery and ferricyanide and ferric EDTA bleach regeneration result in a substantial cost benefit to the facilities using them because of the recovery of raw materials. These recovery operations are an important contributor to the profitability of a facility and are almost universally used in the industry. These costs

were included in this study for the information of those few facilities which do not use these in-process controls. The facilities using advanced in-process controls consisting of silver recovery from wash water, countercurrent washing, and wash water recycle and end-of-pipe treatments consisting of ferricyanide precipitation and wastewater evaporation are doing so for the environmental benefit. There appears to be a net cost benefit for the larger plants which recover silver from wash waters. The remainder of the controls have a negative cost impact.



### SECTION III

#### CHARACTERISTICS OF THE INDUSTRY AND PROCESSES

##### INDUSTRY DESCRIPTION

The photographic processing point source category consists of photographic processing plants processing silver halide sensitized photographic materials to produce continuous-tone black and white or color negatives, positive transparencies, and prints for delivery to external customers. There are approximately 11,000 such photographic processing facilities in the United States found among businesses in four Bureau of the Census Standard Industrial Classification (SIC) codes.

Facilities primarily engaged in photography for the general public are classified as "Photographic Studios, Portrait" (SIC 7221). Included in this group are portrait photographers and school, home, and transient photographers. Establishments engaged in commercial photography are classified in "Commercial Photography, Art, Graphics, and Related Design" (SIC 7333). Facilities primarily engaged in film developing and print processing for the trade or for the general public are included in "Photofinishing Laboratories" (SIC 7395); those engaged in motion picture film processing are classified in "Services Allied to Motion Picture Production" (SIC 7819). The 1972 Bureau of Census determination of the number of establishments classified by each SIC code is given in Table III-1 along with some additional estimates given in the Wolfman Report.

TABLE III-1  
Photographic Processing Establishment Categories

	<u>1972 Census</u>
<u>SIC 7221</u> Photo Studios, Portrait with payroll, oper. entire year	5,466
<u>SIC 7333</u> Commercial Photographic Studios with payroll	2,684
<u>SIC 7395</u> Photofinishing Labs with payroll	1,979
<u>SIC 7819</u> Services Allied to Motion Picture Production, with payroll	855
	<u>Wolfman Report</u>
Major labs (amateur)	600
Professional processing labs	775
School finishers	100

A breakdown of the number of plants and the percentage of total production for five categories of plant size (based on daily production) is shown in Table III-2. The amount of production for each size category is expressed as a percentage of the total U.S. production estimated to be approximately 200 million square meters (2 billion square feet) of processed photographic materials per year. All estimates are based on information collected during this study from various industry sources. The plant size categories and "typical" plant production for each category are used in Section VIII of this report for the development of in-process control and treatment costs.

TABLE III-2

## NUMBER OF PLANTS AND PRODUCTION BREAKDOWN BY SIZE CATEGORY

Production sq m/day (sq ft/day)	Production Size Category	Typical Production sq m/day (sq ft/day)	Number of Plants	Percent Total U.S. Production
<93 (1,000)	<A	9.3 (100)	9,900	12
93-186 (1,000-2,000)	A	139 (1,500)	200	4
186-464 (2,000-5,000)	B	325 (3,500)	305	84
464-4,640 (5,000- 50,000)	C	1,390 (15,000)	200	
4,640-∞ (50,000-∞)	D	6,970 (75,000)	15	

## PROCESS DESCRIPTIONS

Either a two-step or a single-step procedure is used to produce a positive image of the subject on film or paper. In the two-step procedure a chemical process called the "negative" process is used. The first step consists of producing a negative image on film, called a negative transparency, by exposing it to light from the subject and processing the film with the negative process. The transparency is then used as a light mask in the second step to expose paper or film. This material is processed by essentially the same chemical process used in the first step to produce the desired positive image. The single-step procedure uses a "reversal" chemical process which directly produces a positive image of the subject on the film or paper.

The following are detailed descriptions of these negative and reversal processes.

### Black and White Photographic Processing

#### General

Black and white film or paper consists of a base material or substrate, which is coated with a light-sensitive emulsion. Light sensitivity is imparted by distributing silver halide crystals throughout the emulsion. When the emulsion is exposed to a light image, electrons are ejected from the impacted halide atoms. These "free electrons" are in time trapped by crystal imperfections or other chemicals. The electrons attract positively charged free silver ions in the crystal lattice forming clusters of metallic silver at the trap sites. These clusters of metallic silver, still very small, form a latent image of the original light exposure pattern. During processing, the developer solution causes additional silver to be formed at the cluster sites to the extent that the clusters grow, aggregate, and form a visible image, a process of chemical amplification. The film image then undergoes further chemical treatment to stabilize the image and remove excess chemicals. In the reversal process, the additional step of forming the reversal image is required before stabilization.

### Negative Process

The negative process is utilized for producing either a negative or a positive image on film or paper. Three basic chemical processing steps are generally used followed by a clean water wash. These steps consist of development, development stop, and fixing. Often the stop step is omitted, and occasionally an emulsion hardening step is added after the fix.

#### Develop--

The first processing step is developing in which the silver halide crystals in the gelatin emulsion are bathed in a chemical solution, causing the visible image to form. This chemical solution, the developer, contains four primary ingredients:

- (1) A developing agent, usually an organic aromatic compound [e.g., a mixture of hydroquinone and Metol (p-methylaminophenol) or hydroquinone and Phenidone (1-phenyl-3-pyrazolidone)], whose function is to cause the previously formed latent image to grow by reducing additional silver ions at the silver cluster sites;
- (2) An activator or accelerator, commonly sodium hydroxide, sodium carbonate or borax (sodium tetraborate), whose function is to make the developing agent sufficiently active by pH control;
- (3) A preservative, commonly sodium sulfite or sometimes potassium metabisulfite, whose function is to prevent both oxidation of the developing agent and discoloration of the used developing solution; and
- (4) A restrainer, either inorganic (potassium bromide) or organic (benzotriazole), whose function is to prevent the breakdown of the protective layer surrounding each silver halide grain. This reduces fogging caused by development of the unexposed grains.

### Short Stop--

Following the development step, the film is immersed in an acid stop bath which neutralizes and, to some extent, removes the developer absorbed in the emulsion. A dilute solution of a weak acid, e.g., 0.5 percent acetic acid, is usually used.

### Fix--

The fix step removes unexposed silver halide by converting it into a soluble complex. The fixer solution contains either sodium or ammonium thiosulfate ("hypo") as the principal ingredient. Usually sodium bisulfite or potassium metabisulfite is added to cause an acid condition in the solution to neutralize any developer contamination. The sodium bisulfite or potassium metabisulfite also acts to prevent oxidation of the thiosulfate.

### Harden--

This step serves to check emulsion swelling and raise its melting point, thus allowing a higher temperature to be used for drying. Potash alum (potassium aluminum sulfate) is commonly used as the hardening agent though chrome alum (potassium chromium sulfate) is sometimes used. It is common to add the alum compound to the fix solution so that the fixing and hardening are accomplished in a single step.

### Wash--

A water wash is the final solution step. Its purpose is to remove the processing chemicals absorbed in the emulsion or substrate.

### Dry--

The final processing step is drying the photographic film or paper in a dust-free atmosphere.

### Reversal Process

The reversal process forms a direct positive image on the same material used for the original exposure and is most often used for the production of motion picture films and projection slides. It is common to pre-harden the emulsion in the first processing step because more steps are used in the reversal process which tend to soften the emulsion. The pre-hardening solution contains hardening agents such as formaldehyde or succinaldehyde, an antifoggant (6-nitrobenzimidazole and sodium bromide) and sodium sulfate to retard emulsion swelling. After pre-hardening, a neutralizing bath is used to prevent developer contamination. A typical neutralizing solution contains hydroxylamine sulfate and sodium sulfate. The exposed material is fully developed to a negative using a developer solution similar to that used in the negative process except that a small quantity of thiocyanate is added to aid in dissolving small non-light sensitive silver grains. The film is then washed and the silver negative image removed by bleaching in an acidic permanganate or dichromate solution. A clearing bath (for example, bisulfite) is used to remove the bleaching agent and reaction products, leaving the undeveloped silver halide crystals in the emulsion. The emulsion is then given a uniform light exposure, and the remaining silver halide is developed and fixed to provide the positive image. As an alternative to this procedure, a highly fogging developer or non-selective reducer may be used for the second development.

Certain black and white materials, commonly referred to as reversal products, yield a direct "reversal" (positive) image but are processed by the conventional negative process, i.e., no bleach step is used. This is accomplished by incorporating appropriate chemicals into the emulsion during the manufacturing process. These subsequently produce a reversal image during developing.

## Color Photographic Processing

### General

Unmodified silver halide emulsions are sensitive only to a limited range of wave lengths, including the blue-violet region of the visible spectrum, ultraviolet, and shorter wave lengths. However, certain organic dyes can be included in the emulsion to extend sensitivity to longer wave lengths through the visible spectrum into the infrared or to make the emulsion sensitive to a particular region of the visible spectrum. Color films have three separate light sensitive emulsion layers, which after inclusion of the appropriate dyes, record an image of the blue light components on one layer, the green light components on another, and the red light components on the third layer.

The commonly used color materials are color negative film, color reversal film, color print film, and color print papers. The three basic processes for the processing of color materials are negative, reversal with couplers in the emulsion (IC), and reversal with coupler in the developers (DC). The commonly used color materials, uses, and process types are given in Table III-3.



TABLE III-3  
Common Color Materials

<u>Color Material</u>	<u>Use</u>	<u>Process</u>	<u>Image</u>
negative film	original exposure, intermediate for copying positive trans- parencies	negative	negative
positive print film	positive transparency from negative film	negative	positive
reversal film	original exposure, intermediate	reversal (IC) or reversal (DC)	positive or negative
positive print paper	print from negative film	negative	positive
reversal paper	print from positive transparency	reversal (IC)	positive

Descriptions of these color processes follow. They apply to both film and paper base materials as the steps and chemical solutions are basically the same for each. Where major differences occur, they are noted.

#### Color Negative Process

The first step in the negative process is color development. Color development produces in each layer a dye image and a silver image, the amount of dye generated being proportional to the silver developed. The images are negative with respect to the exposure sources. The dye image is formed by a reaction between the developer oxidation products and a group of organic molecules called couplers to form dyes of the appropriate color in each layer. The developer solution commonly contains salts of diethylpara-phenylene diamine or its derivatives as the developing agent. The salts may be the hydrochloride or the sulfate. Certain newer developing agents, such as 4-amino-N-ethyl-N-[beta-methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate,

produce better color rendition and have reduced toxicity. In addition to the developing agent, the developer solution usually contains color-fog restrainers such as hydroxylamine hydrochloride, a solvent such as benzyl alcohol and a contrast and color balance control agent such as ethylenediamine tetraacetic acid or citrazinic acid.

The next process step stops development and removes excess developer. This can be done by washing, but usually a weak acid stop bath is used, e.g., 0.5 percent acetic acid buffered with sodium acetate to control pH, followed by a brief wash. In some cases a stop bath is used with a hardening agent.

The film or paper is then bleached to convert the developed silver image back to a silver halide in preparation for the subsequent removal of all silver from the final product by the fix solution. The color dye image remains unaffected in each layer. The bleach most commonly used in the negative process is the ferric salt of ethylenediamine tetraacetic acid (ferric EDTA). It is possible to substitute ferricyanide bleach for the ferric EDTA in some processes. This is done by some large plants incorporating centralized ferricyanide bleach systems which supply bleach to multiple processes.

After bleaching, the film or paper is fixed to remove the silver compounds and washed to remove all excess chemicals. Finally the emulsion is hardened and stabilized using a 2 percent formalin and 3 percent sodium carbonate solution, with the formalin acting as the dye stabilizer. Most color paper processes use a combination bleach-fix solution which converts silver to the halide and dissolves the halides in one operation. The typical solution contains ferric EDTA and sodium thiosulfate as major ingredients.

### Color Reversal Processes

There are two different types of color reversal materials. In one, the color couplers which form the color dye image are incorporated into the emulsion layers at the time of manufacture (IC). Most color reversal materials are of this type. The second type has three black and white layers,

each sensitive to a different color. For this type of material, the color couplers are added during development (DC). The (IC) process applies to film and paper materials, and the (DC) process applies to film. The procedures and chemistry for reversal color processing are described below.

#### Color Reversal Process (IC)--

The first step in the color reversal process for (IC) materials is to pre-harden and develop the film or paper in a highly alkaline negative developing solution to produce a negative silver image in each layer. This developer is similar to that used for black and white reversal development. Color couplers are not affected during this step. A small amount of thiocyanate added to the developing solution aids in dissolving small, non-light sensitive silver halide grains, thus eliminating a source of image fog. Following the negative development step, the material is washed or treated in stop and hardening solutions. The emulsion is then re-exposed to a strong light source, exposing the undeveloped silver halide. The material is further developed in a color developer solution which reduces the remaining silver halide to silver and reacts with the couplers to produce a positive dye image of the appropriate color in each of the three layers. The color developer formulation is similar to the developer used for color negative materials. In some processes, a highly fogging color developer is used in place of the light re-exposure. The dye development is usually followed by hardening, stop and wash steps, which in turn are followed by bleaching. A commonly used film bleach is a potassium ferricyanide and potassium bromide solution which converts the developed silver to silver bromide. EDTA bleach is also used for certain film processes, and an EDTA based bleach-fix is commonly used for reversal papers. The film or paper is then fixed to remove the silver bromide, washed, stabilized, and dried.

#### Color Reversal Process (DC)--

Color reversal (DC) film processing is complicated and requires rigorous chemical control of solutions. The first development step, as with the reversal (IC) materials, forms

a negative silver image in all three layers. After this, all three layers in the emulsion are treated separately. First, the red-sensitive layer is prepared for development by exposure to red light through the base of the film. This exposes the remaining undeveloped silver halide in that layer. The other two layers, which are not sensitive to red light, are unaffected. The film is treated with a color developer that contains, among many other ingredients, a coupler which forms a red-absorbing (cyan) dye in the red-sensitive layer. As the color developing agent reduces the silver halide and forms an image, the oxidized color developer in the vicinity of the developed silver grains forms the positive cyan dye image.

After washing, the film is exposed from the top with blue light exposing the undeveloped silver halide in the top blue-sensitive layer. A yellow filter layer protects the middle green-sensitive layer. A second color developer, containing a soluble yellow coupler, produces both a silver and blue-absorbing (yellow) positive dye image in the top layer.

After a second wash, the middle layer is developed and chemically fogged in a third color developer containing a fogging agent and a magenta coupler which forms the final positive silver and green-absorbing (magenta) dye image. The film at this point has a negative silver image, a positive silver image, and a positive color dye image in each layer. Following a third wash, the silver images are removed as in the other color processes by bleaching and fixing followed by washing and drying.

#### PROCESSING CHEMISTRY

To make up the required solutions for processing a particular film or paper, the processor has a choice of (a) using a kit where all the necessary solution formulations are included, (b) using bulk formulations for each solution, or (c) using bulk raw chemicals. In general, small processors use kits and larger processors use bulk formulations and raw chemicals. The processor has a wide latitude in selecting formulations for the processing of black and white materials. For example, many different

developer formulations made by any one of several manufacturers can be used to develop a given black and white film. In color processing, the choice is more limited, because process solutions are formulated specifically for a particular emulsion type.

Because of the broad range of black and white processing formulations, individual processes are not identified by name; rather, formulations are named by the various manufacturers (for example, developers such as Dektol, D-76, 53-D, etc.). In color processing, where each solution formulation is more limited, the processes generally have names which define the process steps and the solution formulations. For a given color emulsion, several manufacturers may provide kits or formulations with different names, but the chemical content is quite similar.

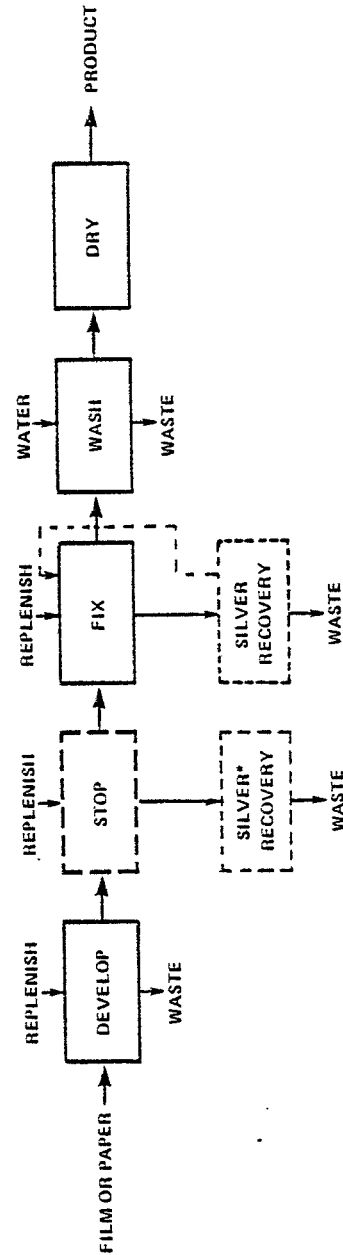
In references to black and white processing in this report, no process names are used, only the descriptors, negative or reversal. Where appropriate, color processes are referenced by name. The process name is used to identify a specific composition and sequence of processing solutions for which certain photosensitive materials are designed. Any manufacturer of photosensitive materials may produce films or papers designated for processing in any specific process. Any manufacturer of photographic chemicals may produce chemicals intended to be used for specific processing solutions in any designated process. The following is a list of the color processes most often encountered during this study.

<u>Material Type</u>	<u>Process Name</u>
Color negative process film	C-22, C-41, MC-42, ECP-1, ECP-2 ECN-1, ECN-2
Color reversal process film (IC)	E-3, E-4, ME-4, EM-25, CRI, ECO-3, E-6, E-7M, EA-5
Color reversal process film (DC)	K-12, K-14
Color negative process paper	EP-2, EP-3, MC111, 85/86
Color reversal process paper	EPR-5, EPR-100, P-10 P-18

Over the period of this study the manufacture of photographic materials designed for some of these processes has been discontinued. As the stocks of these materials are depleted there will no longer be a need for the corresponding processes. The processes included in this category are C-22, ECN-1, E-3, E-4, K-12, and EPR-5.

The schematic process diagrams for the listed processes are included in Figures III-1 through III-19. Dashed lines represent optional steps or operations. The optional recycle of fix is applicable only when electrolytic silver recovery methods are used. The additions of make-up chemicals, regeneration chemicals, or air required in the various bleach regeneration processes are not shown in the following schematics. This information is given in the discussion of the regeneration methods in the following subsections.

The process solution chemicals lose activity, are transformed by chemical reaction, and are contaminated by chemicals from the emulsion and by drag-in from previous solutions. There is also volume reduction or concentration changes due to absorption of solution into the emulsion and evaporation. Drag-in and drag-out of solution are usually not factors because they are approximately equivalent and cause no net volume change. To alleviate the effects of chemical transformation and volume reduction, it is common practice to replenish the solutions with fresh or



\*SILVER IS RECOVERED FROM THE STOP BATH RATHER THAN THE FIX IN CONTINUOUS MACHINES THAT PROCESS BLACK AND WHITE NEGATIVE ROLL PAPER USING A DEVELOPER, STOP, AND FIX; WHEN ONLY A DEVELOPER AND FIX ARE USED, SILVER IS RECOVERED FROM THE FIX.

FIGURE III-1. PROCESS: BLACK AND WHITE NEGATIVE -- FILM AND PAPER





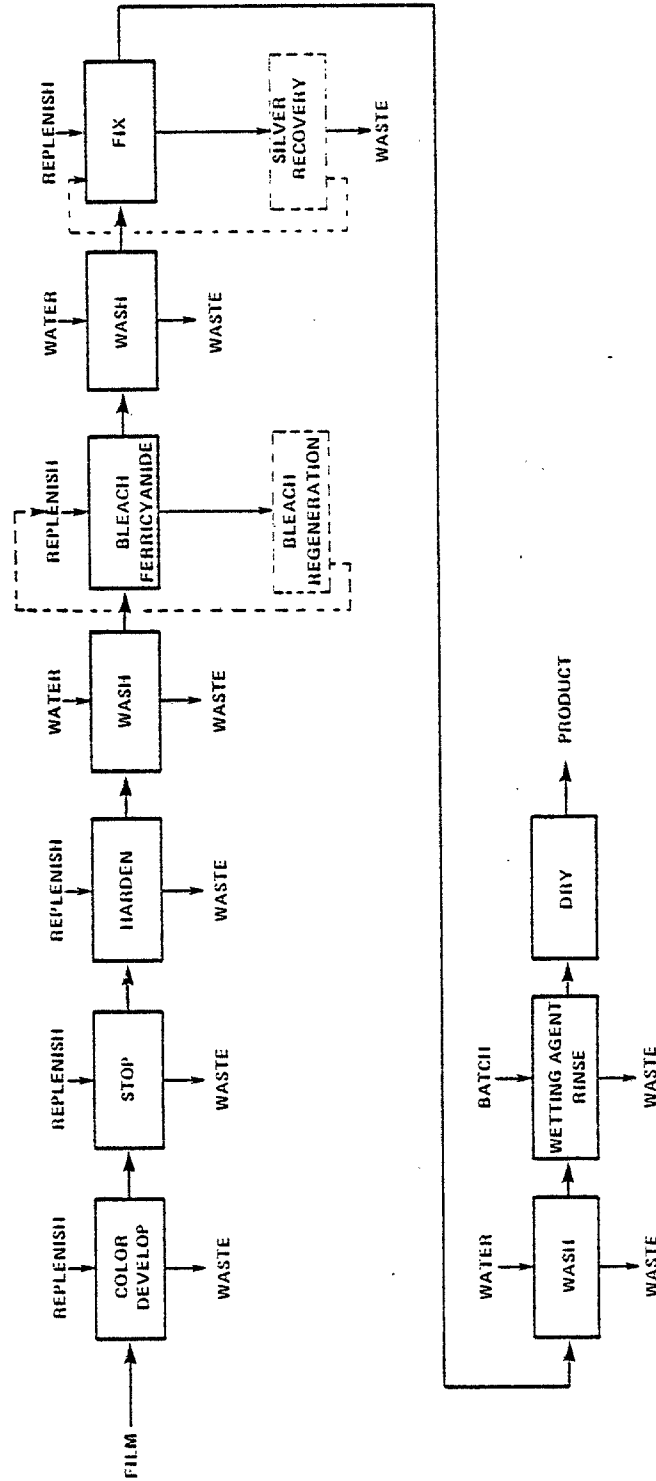


FIGURE III-3. PROCESS: COLOR NEGATIVE FILM, C-22

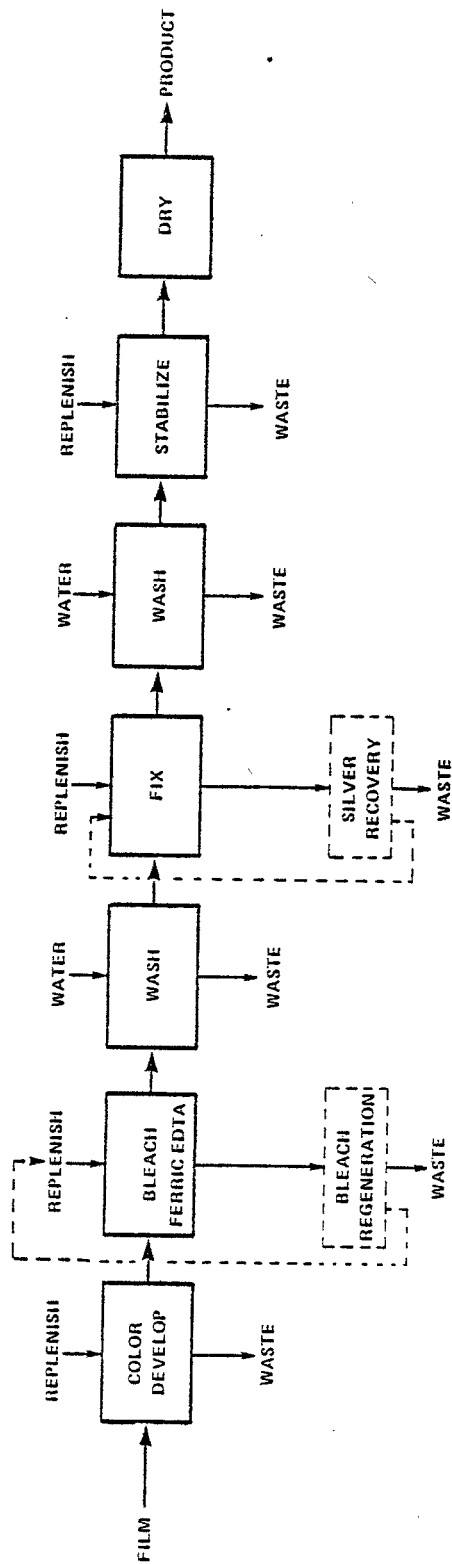


FIGURE III-4. PROCESS: COLOR NEGATIVE FILM, C-41

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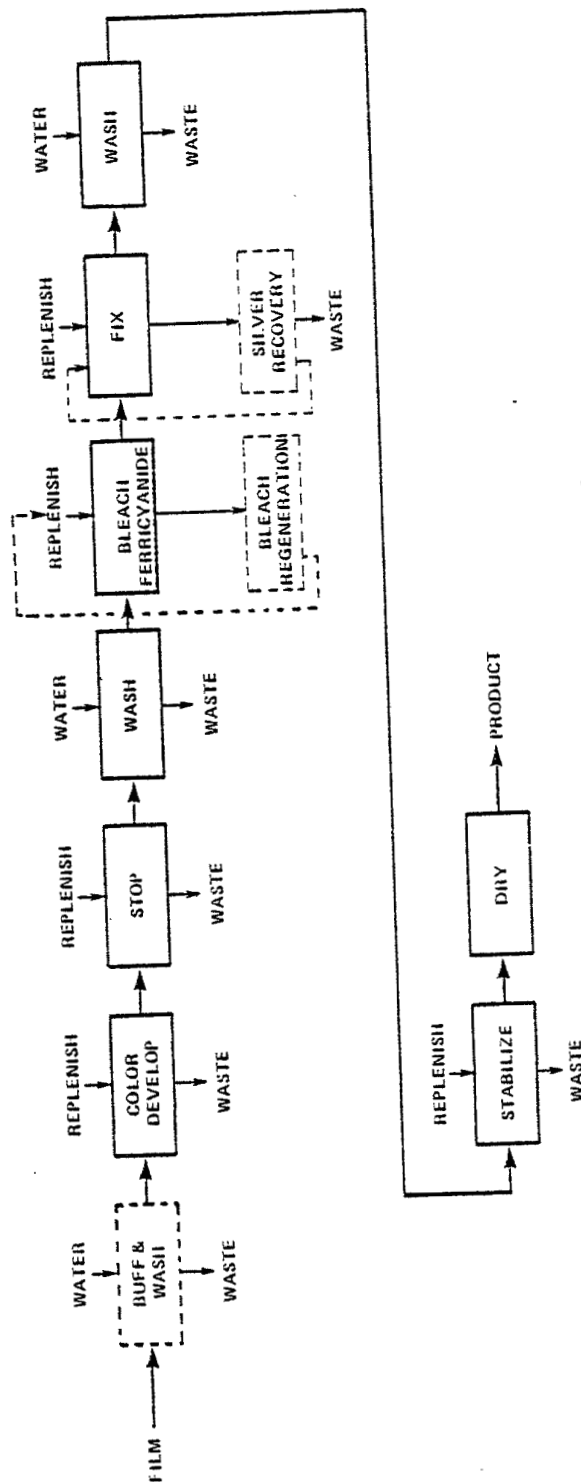
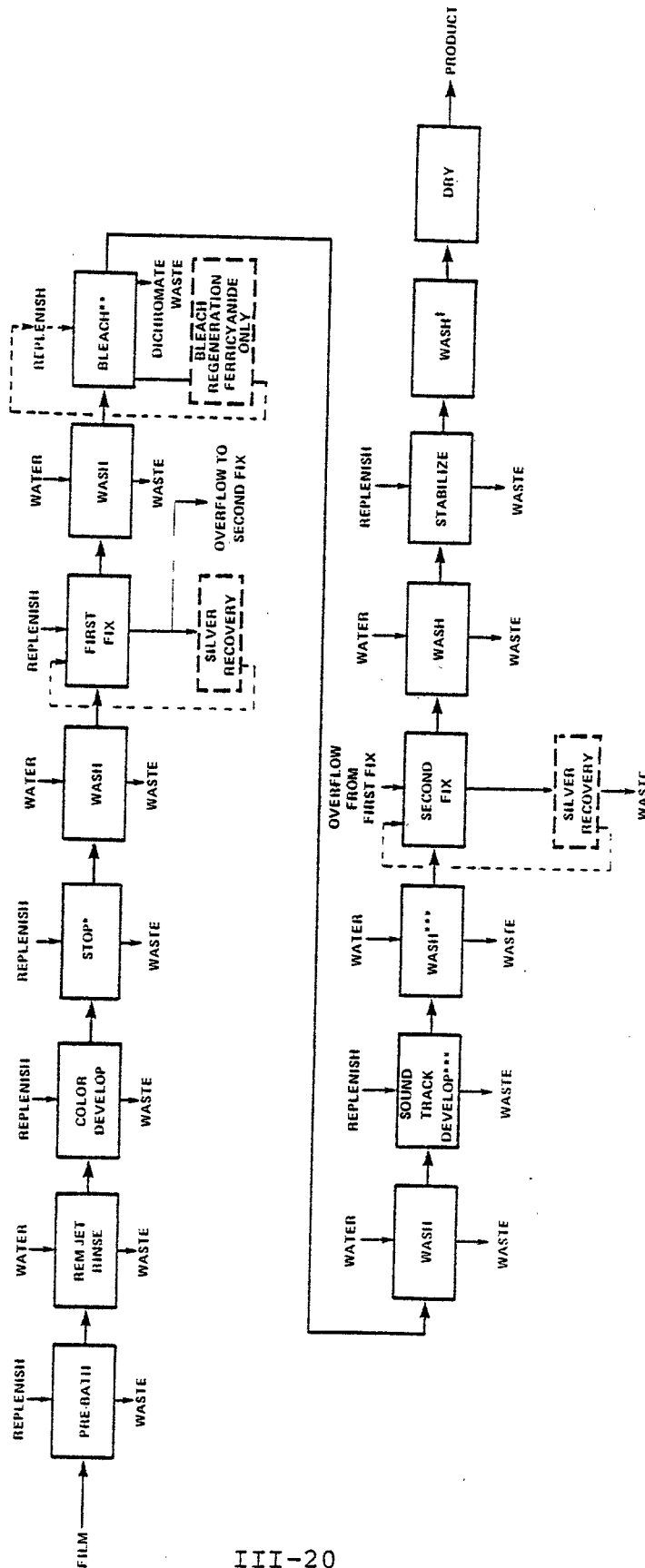


FIGURE III-5. PROCESS: COLOR NEGATIVE FILM, MC-42



\*STOP USED FOR ECP 2 ONLY

\*\*FERRICYANIDE BLEACH USED FOR ECP 1, ECP 2, DICHLOROMATE BLEACH USED FOR ECP 1

\*\*\* USED ONLY FOR OPTICAL SOUND TRACK PRINTING

† USED FOR ECP 1 ONLY

FIGURE III 6. PROCESS: COLOR NEGATIVE FILM; ECP 1, ECP 2

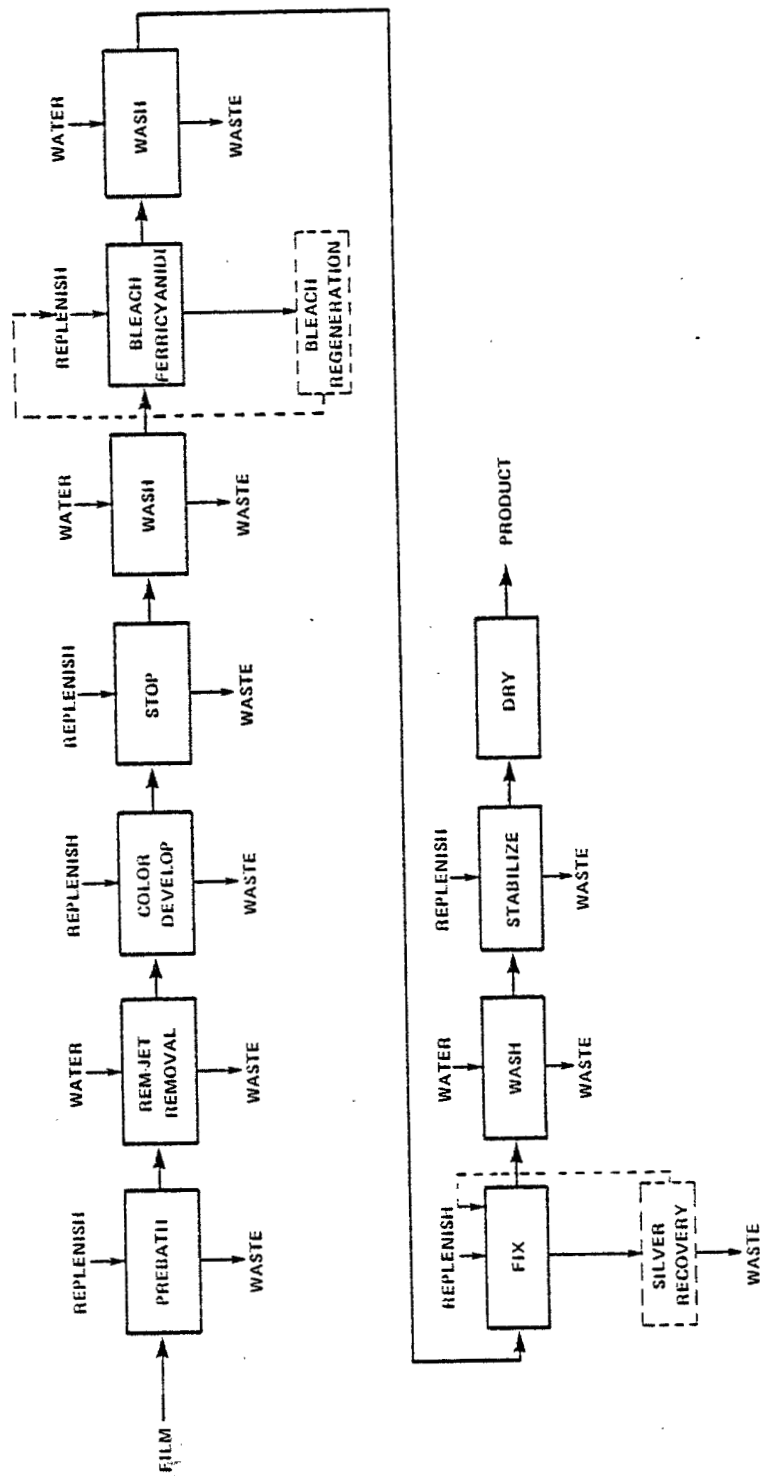


FIGURE III-7. PROCESS: COLOR NEGATIVE FILM, ECN-2

45

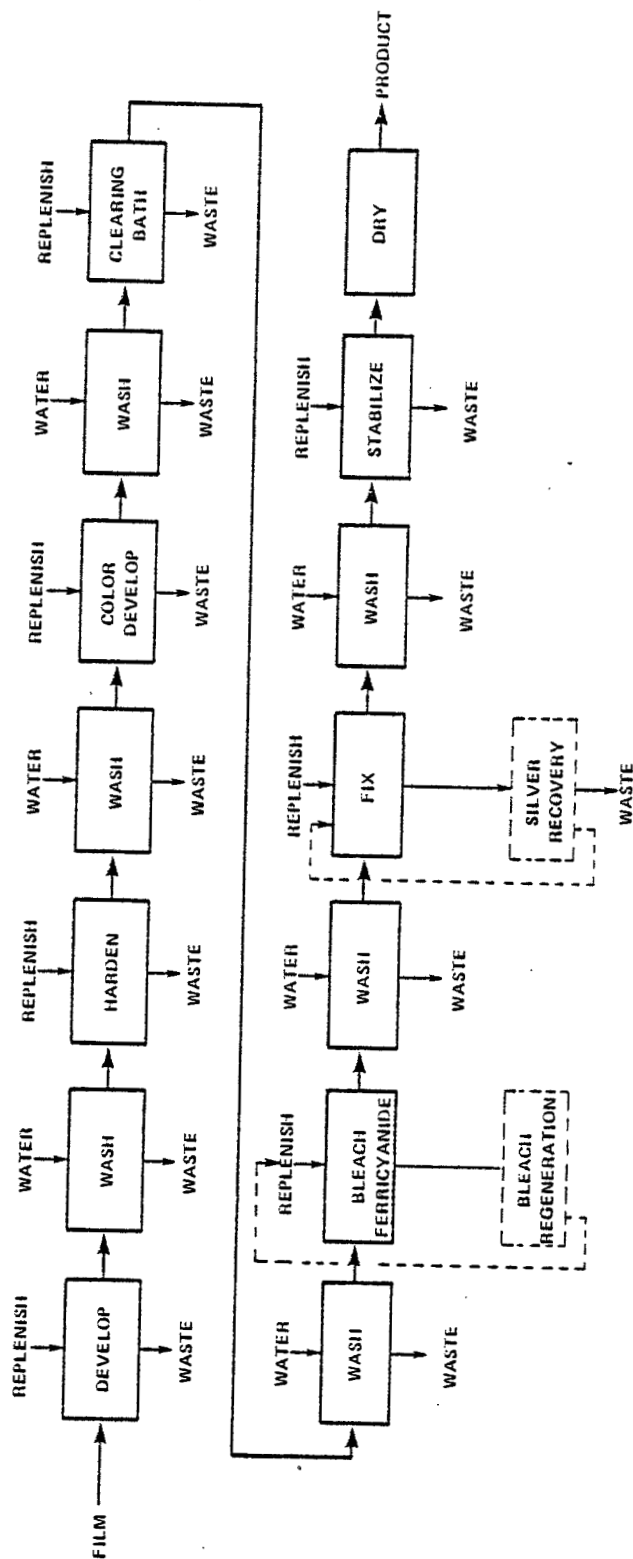


FIGURE III-8. PROCESS: COLOR REVERSAL FILM (IC), E-3



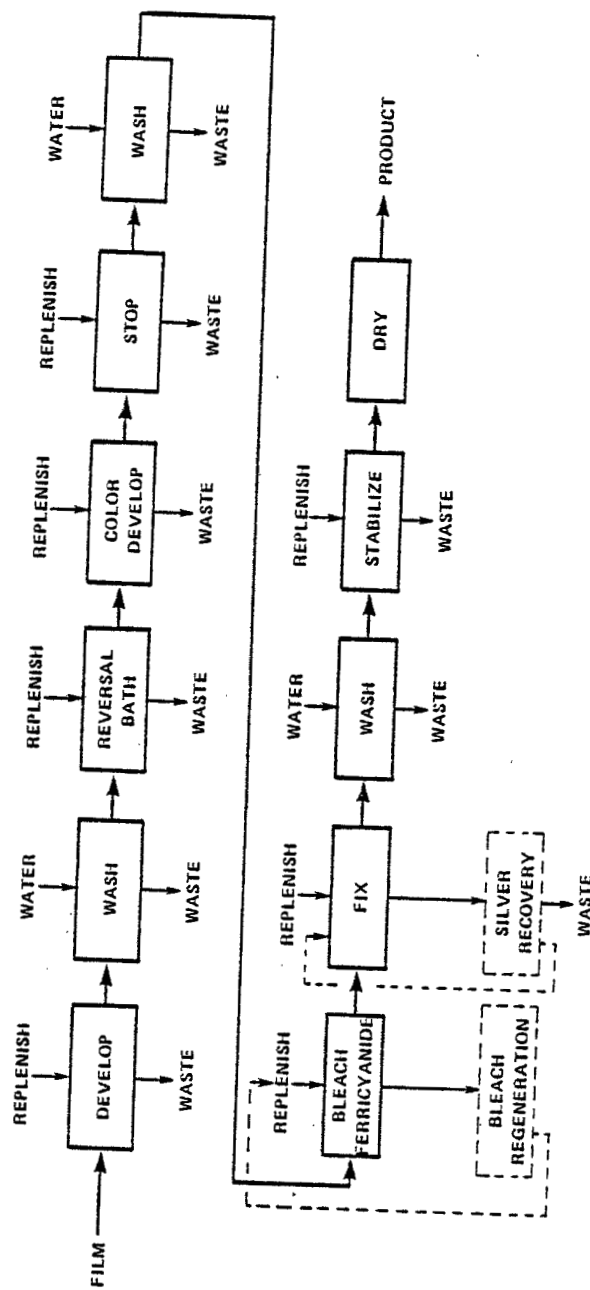
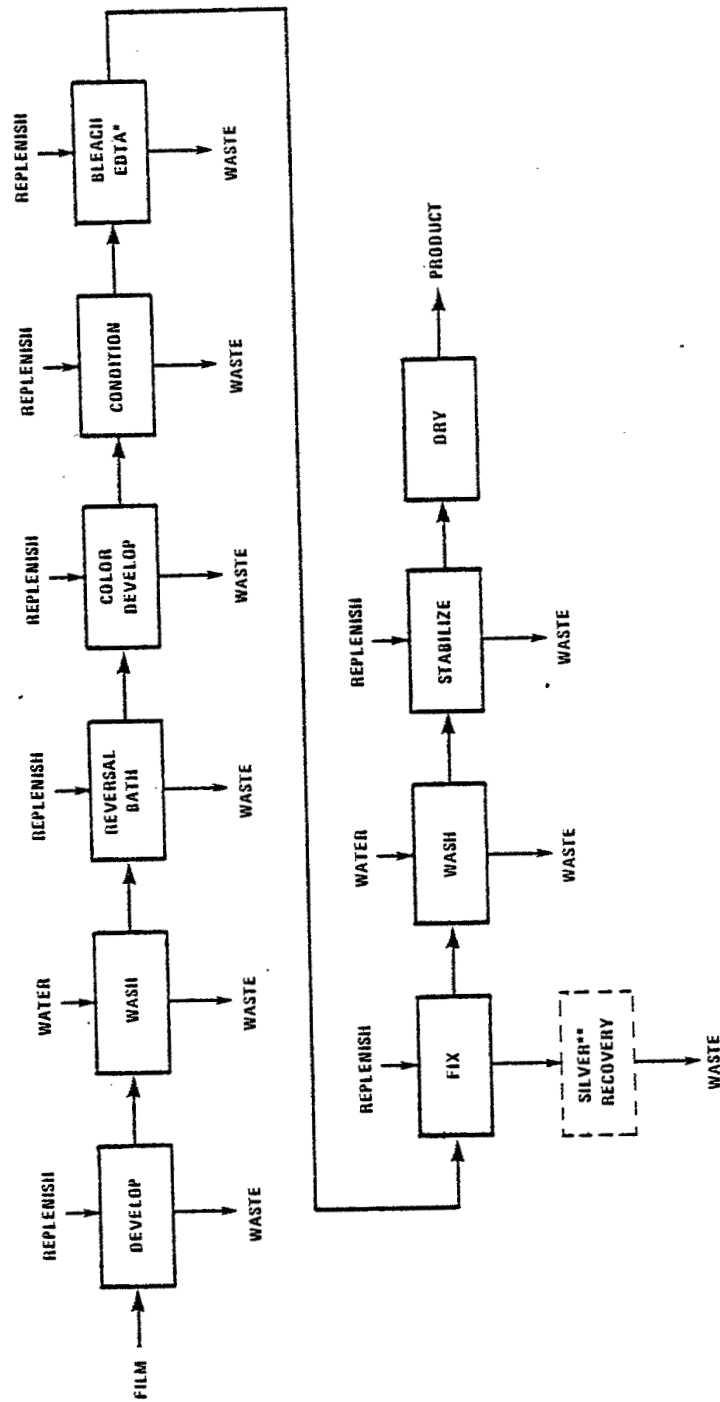


FIGURE III-10. PROCESS: COLOR REVERSAL FILM; (IC), E-7M





\*NO REGENERATION OF BLEACH  
 \*\*NO RECYCLING OF FIXER BECAUSE OF BLEACH CONTAMINATION

FIGURE III-11. PROCESS: COLOR REVERSAL FILM; (IC), E-6

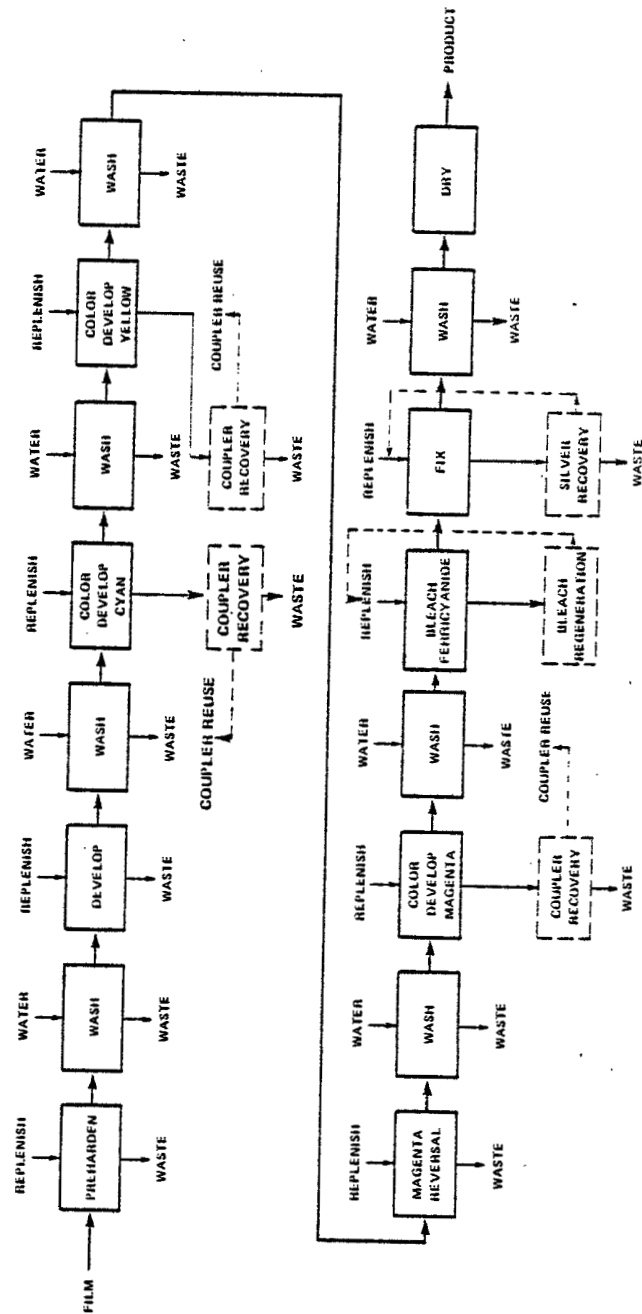


FIGURE III-12. PROCESS: COLOR REVERSAL FILM (DC), K-12

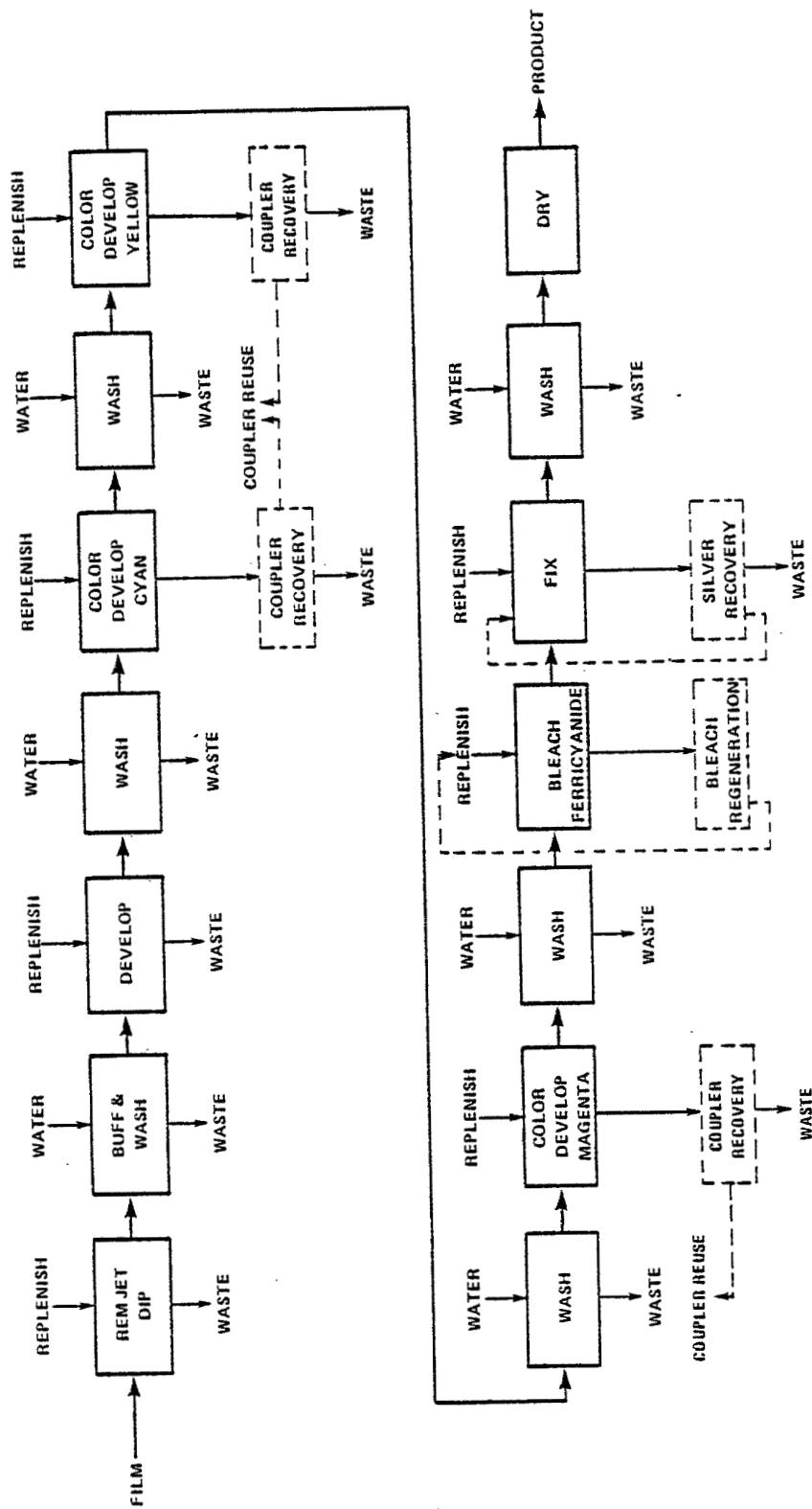
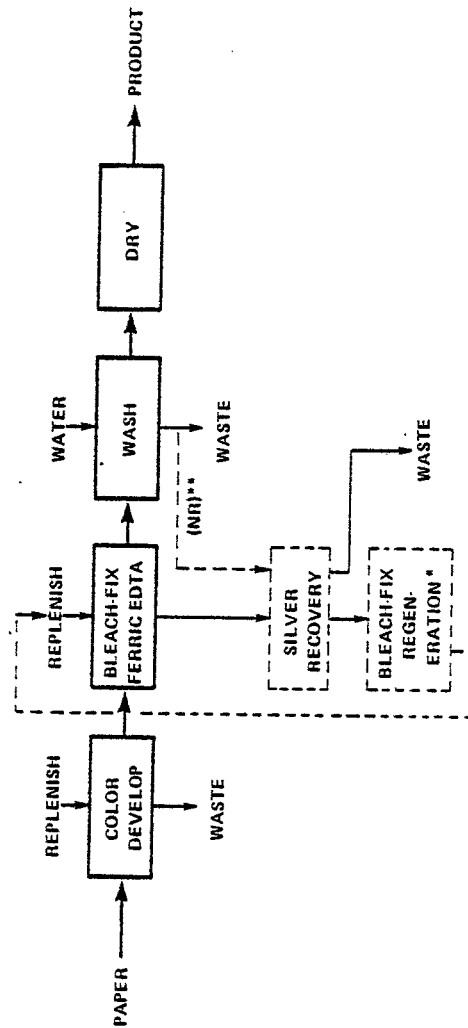


FIGURE III-13. PROCESS: COLOR REVERSAL FILM (DC), K-14

III/27  
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\*NO REGENERATION WITH NR BLEACH FIX  
 \*\*SILVER RECOVERY FROM WASH USED IN EP-2 PROCESS WITH NR BLEACH FIX

FIGURE III-14. PROCESS: COLOR NEGATIVE PAPER, EP-2

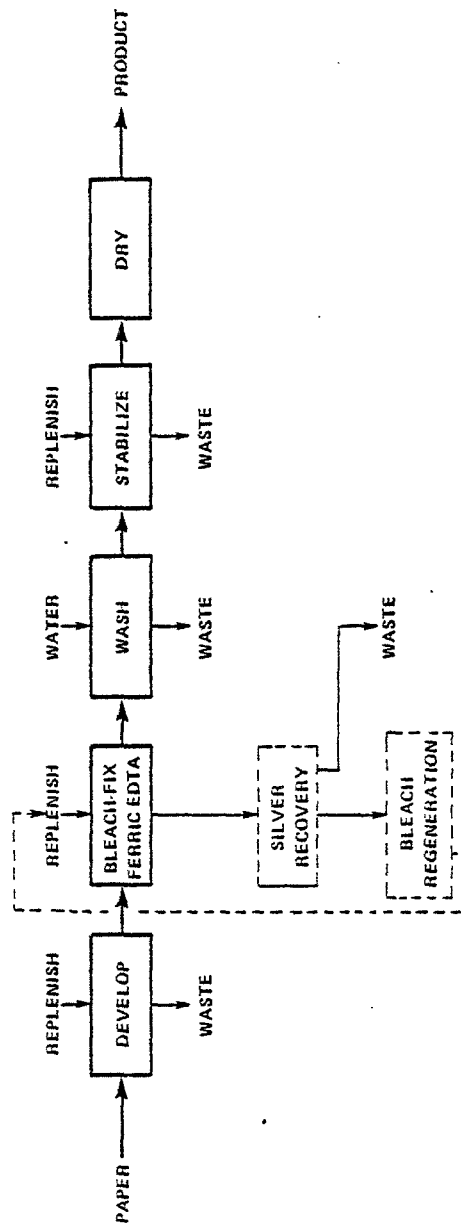


FIGURE III-15. PROCESS: COLOR NEGATIVE PAPER: EP-3, 05/06

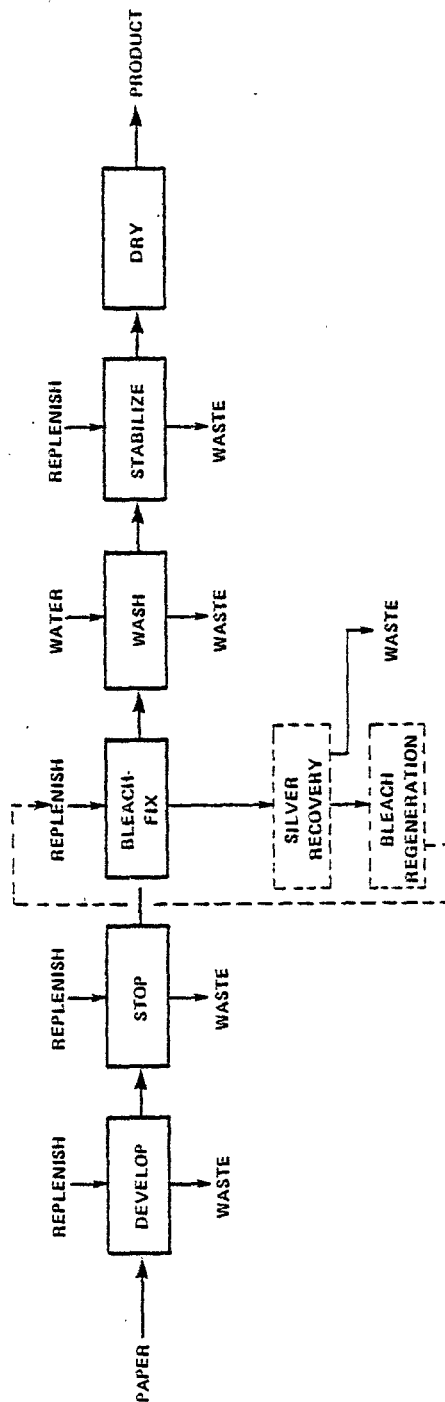


FIGURE III-16. PROCESS: COLOR NEGATIVE PAPER, MC 111

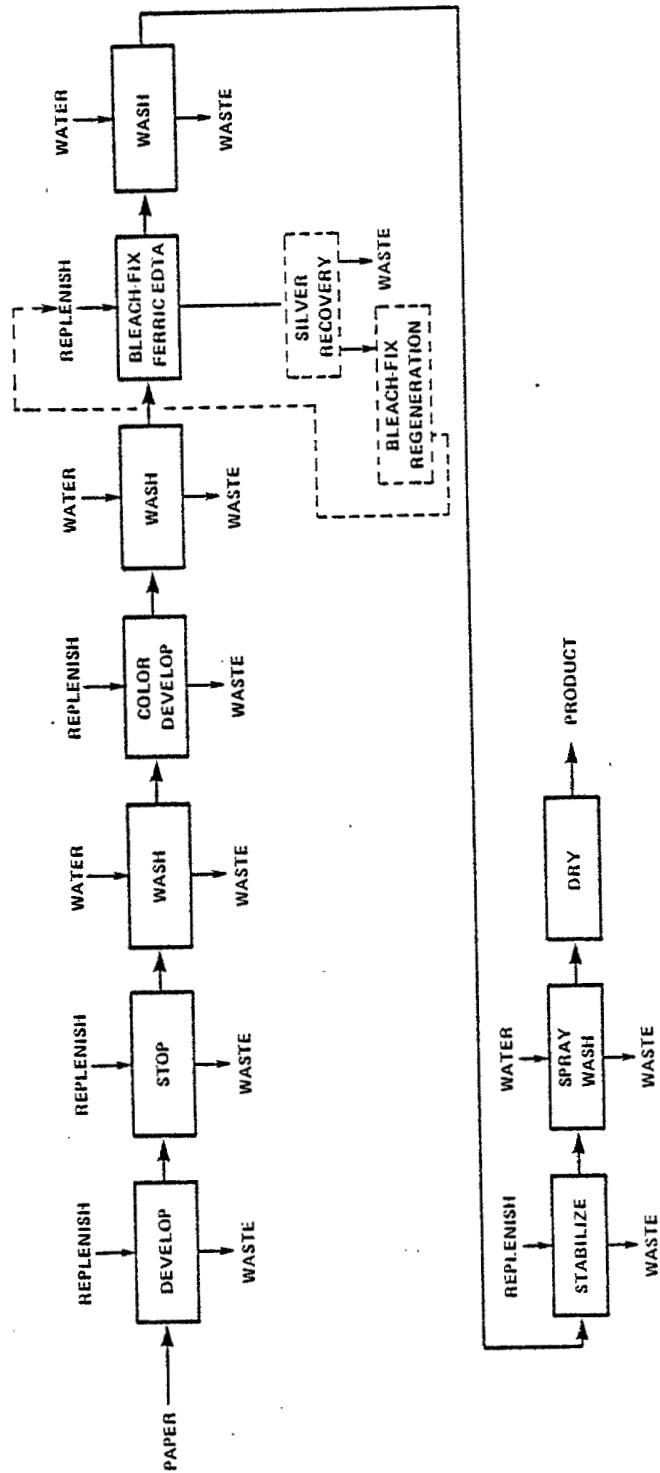


FIGURE III-17. PROCESS: COLOR REVERSAL PAPER, EPR-5, EPR-100

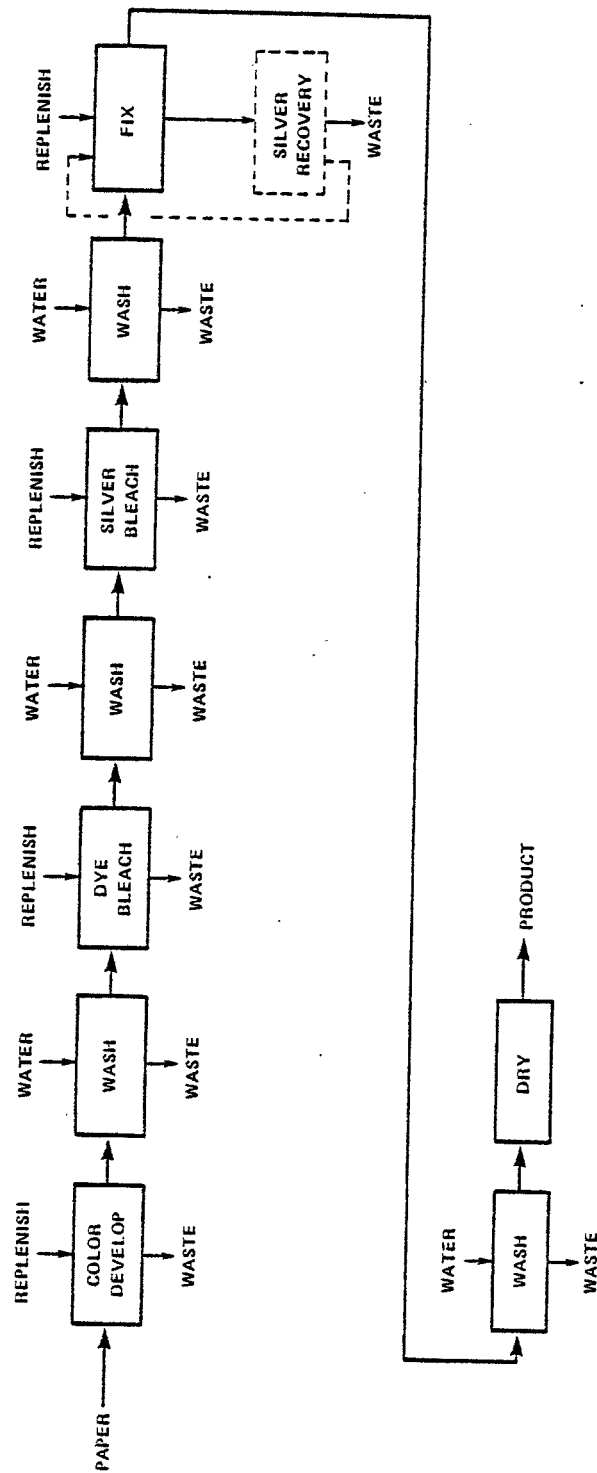


FIGURE III-18. PROCESS: COLOR REVERSAL PAPER, P.10



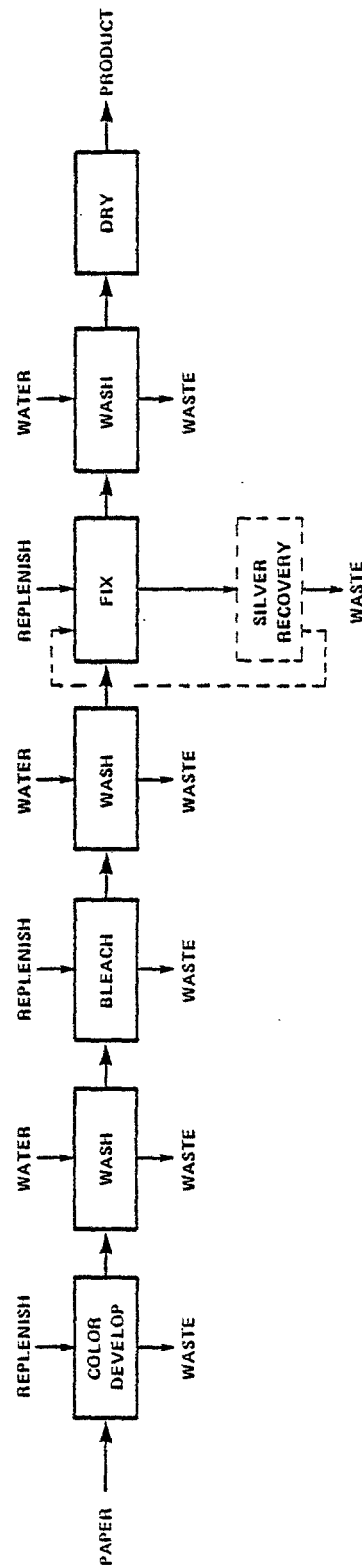


FIGURE III-19. PROCESS: COLOR REVERSAL PAPER, P.18

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reconstituted chemicals. For example, with use, a developer gradually loses its effectiveness. The concentration of the developing agent and the pH decrease, and the halide ion accumulates. The developer replenishing solution usually contains a higher concentration of developing agents than the original solution and little or no bromide. It also contains alkali to help maintain a constant pH.

The replenishment is at a continuous or programmed rate on continuous process machines. The rate of replenishment is greater than the normal volume reduction resulting in an overflow of solution. This reduces accumulation of unwanted chemicals in the process tank. Batch replenishment may be used on "dip and dunk machines" or with manual processing.

Some processors practice a type of replenishment called "replenishment on demand" whereby the critical constituents (for example, chromate) of the solution are monitored and replenishment is done by batch in the required amount when these constituents are reduced to predetermined levels. Although overflow is still allowed to occur to reduce unwanted chemical accumulation, proponents of this method claim that the waste load is reduced from that found in continuous replenishment because of higher efficiency. A further explanation of this method is given in a subsequent section of this report, Reconstitution of Dichromate Bleach.

## PROCESSING EQUIPMENT

Photographic materials may be processed either manually or in automatic processing machines. Manual processing and certain automatic "drum" machines are suited to custom processing or processing small quantities of material. Manual processing is predominately suited to very small labs but may be found in the larger labs as well. Automatic processing machines (with the exception of drum processors) have the capability for high production rates and are suited to the larger labs.

A manual processing method, sometimes called "sink line" processing, consists of manually placing, for the correct time and in proper sequence, exposed photo material in each of a series of trays or tanks containing the required

chemical solutions. A second manual technique utilizes a single tank or drum. The photo material is placed in the tank or drum and the first processing chemical solution is poured into the container. After remaining for the proscribed time, the solution is dumped and replaced with the second solution. This process is continued until all solutions have been used. An automated version of this process, called automatic drum processing, consists of a motorized rotating drum and preprogrammed, electrically operated solution fill and dump valves.

Most photoprocessors, as included in this study, handle large quantities of film and paper with automatic processing machines. The three types most widely used are "dip and dunk," roller transport, and continuous length processors.

The "dip and dunk" processor, an automated version of "sink line" processing, is generally used for roll films. The machine consists of a series of deep tanks, elevator or lifter mechanisms, and a movable track or chain drive. The film is attached to hangers, automatically transferred from tank to tank by the lifter mechanism and deposited in the tank by the movable track. A limited adjustment of the processing times in individual tanks is possible. The film is dried in a drying tunnel that is part of the machine. A second type of dip and dunk processor is an automatic version of manual basket processing. The film, plates or paper are loaded onto reels or baskets. The entire assembly is moved on an overhead gantry that raises and lowers the basket into each process tank at preprogrammed times.

Roller transport machines consist of a series of solution tanks and use a combination of pinch rollers and belts to feed the photo materials through each solution tank in succession. Roller transport machines are commonly used for sheet film, narrow widths of professional and aerial film and large format (up to 1.3 meters wide) prints. They require no leader and are suited to the processing of single pieces of film or paper at high production rates.

The continuous length processor is generally used for movie films and long rolls of film and paper. Short rolls can also be accommodated by splicing the short rolls together

end on end to make a long length. The continuous length processor consists of a series of deep tanks, roller racks or transports in each tank, and feed and take-up mechanisms. The feed and take-up mechanisms usually include a slack box to facilitate splicing without stopping the main drive. The film travels back and forth in each processing tank over a series of rollers on the rack. The path length and linear film speed are adjusted to give the desired residence time in each tank. Upon exiting a tank, the film travels to the next tank over roller connections between racks. Continuous processing units are time-consuming to thread and are commonly threaded with leader stock. The starting end of a material to be processed is attached to the leader end which then guides the material through the machine. New leader is attached to the end of the processed material and remains in the machine ready for the next run. It is common to run leader before and after production runs for quality control purposes to inspect for mechanical abrasion problems and chemical balance. A short photosensitive test strip is attached to the leader for the chemical balance check. During leader run there is generally either no replenishment or reduced rate replenishment of some solutions. Wash water usually runs at the normal production rates. The wastewater hydraulic load is comparable to production loads. Pollutant loading is reduced to essentially that caused by solution carryover into the wash waters. No additional silver loading occurs since the leader has no silver emulsion.

The ratio of leader to production varies widely and depends on the machine type and the materials processed. "Dip and dunk" machines require no leader. Roller transport machines have pinch roller feed guides which require no leader. Plants that predominately use these machines have a very low leader to production material ratio. On the other hand, plants using continuous machines and processing amateur materials consisting of short lengths of narrow film and paper may have a leader to production material ratio of one or more, i.e., they may run more leader than production material. If possible, the processor will splice the short film end on end to create a long continuous length and reduce the need for leader. However, this is often not possible because of the promise to the customer to return the finished product quickly. A quick turnaround time

requires machines to be continually "at ready," resulting in numerous short runs, relatively large amounts of leader run and frequent quality control checks. The movie labs, which use similar machines and process similar film widths, have leader to film ratios on the order of 0.1 to 0.5 because they process comparatively long lengths and can plan their production more efficiently.

Most automatic processing machines have automatic agitation and solution replenishment. The method most commonly used for agitation is called gas-burst agitation which consists of releasing gas through tiny holes in a distributor plate in the bottom of the solution tank at controlled intervals. The gas bubbles formed during release provide the random agitation pattern necessary for uniform results. Oil-free compressed air is usually used except in the developers where nitrogen is used to prevent oxidation of developing agents.

#### IN-PROCESS CONTROL TECHNOLOGIES

In-process controls are used in the photographic processing industry primarily for the conservation or recovery of raw materials for economic purposes and secondarily for pollution abatement purposes. Controls include: (1) the recovery of raw materials such as silver and organic couplers, (2) the regeneration of processing solutions for recycle such as fix and bleach, and (3) various housekeeping practices such as water saver controls and squeegees.

#### Effect of In-Process Controls on Product Quality

In the consideration of in-process controls, which involve the reuse of solutions, recycle of wash water, or other modifications of standardized procedures, two major precautions should be taken to ensure that (1) the control is properly applied and (2) once applied, the control is properly maintained. Any of these controls, if not properly applied and maintained, can cause immediate or long-term, adverse effects on product quality. For example, dirt build-up can immediately cause pinholes, spots, and scratches; trace chemical build-up, improper chemical balance in the solution, and insufficient chemical removal

from the emulsion can cause (1) stains and improper color balance in the short term and (2) poor dye stability and stains in the long term.

The first precaution concerns proper application of the in-process control on a process specific basis, i.e., successful application on one particular process does not guarantee success on another. When a control is applied to a particular process, it should be established, by testing product quality, that there are no short- or long-term adverse effects. The short-term tests include inspection for stains, spots, and scratches; color balance checks against standards; and hypo retention tests. Long-term effects are somewhat more difficult to evaluate. Current techniques involve subjecting processed test material to accelerated aging conditions prior to performing quality tests.

The use of many of the various in-process controls, which are discussed in detail in the following subsections, has been demonstrated and accepted. Ferricyanide and EDTA bleach regeneration have been established on most color processes, and fix recycling has been successfully used on many processes. On a more limited basis, countercurrent washing and wash water recycle have been established for some processes. Developer recycle has been successfully used on a few color paper processes. Low flow prewash is still being evaluated.

The second precaution concerns proper use and maintenance of the in-process control to ensure continued high standards of product quality. In some cases, strict adherence to recommended maintenance and use procedures may be sufficient to ensure a quality product. In others, careful chemical monitoring of process solutions or wash water and periodic product tests may be required in addition to in-process control equipment maintenance and use requirements. (Note that in-process control use procedures may require chemical monitoring of some solutions.) Finally, the origin or end-use of the material being processed may have some bearing on the use of a particular in-process control. Solution regeneration and wash water recycle do increase the risk of reduced long-term stability or product damage. In

cases where a process is used for unique film originals or where the product must have archival storage capability, the risks imposed by use of an in-process control may be unacceptable.

### Silver Recovery

Two photoprocessing waste solutions contain essentially all silver removed during processing: (1) the fix or bleach-fix overflow and (2) the post-fix wash water.

The state-of-the-art of silver recovery from the fix and bleach-fix processing solutions includes metallic replacement, electrolytic recovery, and chemical precipitation. Ion exchange and reverse osmosis are other methods that can be used alone or in combination with conventional silver recovery systems. However, these are generally considered suitable only for dilute solutions of silver, such as the polish desilvering of effluent from a silver recovery unit or wash water desilvering.

These silver recovery systems can be used in a variety of ways. It is typical to have a primary silver recovery unit, which removes the bulk of silver, in combination with a "tailings" unit. Tailings consist of the relatively low silver concentration effluent from a primary silver recovery system. A tailing unit is used as a secondary or polishing unit for additional silver recovery. The typical system consists of an electrolytic primary unit and a metallic replacement tailing unit. A silver recovery system can be devoted to a single process line or be used to remove silver from the fix from several or all process lines in a plant. The multiple use systems are found in the larger plants. Sometimes a separate fix system is used for processing unique original film to reduce the possibility of inter-process contamination (when desilvered fix is recycled to the process) and the resultant damage to irreplaceable originals.

### Metallic Replacement

Metallic replacement occurs when a metal, such as iron, comes in contact with a solution containing dissolved ions

of a less active metal, such as silver. The dissolved silver, which is present in the form of a thiosulfate complex, reacts with solid metal (iron); the more active metal goes into solution as an ion, and an ion of the less active metal becomes solid metal (silver).

Silver ions will displace ions of many of the common metals from their solid state. Because of its economy and convenience, iron in the form of steel wool is used most often. Zinc, as a replacement metal, can also be effective, but it is not used because of its relatively higher toxicity and greater cost. Aluminum has also been used as a replacement metal but is not commonly used because the simultaneous generation of hydrogen gas could be hazardous.

For most efficient operation, the pH of the solution passing through the metallic replacement unit should be between 4 and 6.5, with an optimum between 5 and 5.5. Below a pH of 4, the dissolution of the steel wool is too rapid. Above a pH of 6.5, the replacement reaction may be so slow that an excessive amount of silver would be lost because of the long reaction time required.

Silver recovery by metallic replacement is most often carried out using commercially available units consisting of a steel wool filled plastic bucket with appropriate plumbing. Typical practice is to feed waste fix to two or more canisters in series or series-parallel combinations. For two canisters in series, the first canister removes the bulk of the silver and the second unit polishes the effluent of the first and acts as a safety factor if the first unit is overused. When the first unit is exhausted, it is common to replace it with the second and put a new unit in the place of the second. Silver concentrations in the effluent from a single unit average 40 to 100 mg/l over the life of the unit versus a range of 0.1 to 50 mg/l when two canisters are used in series.

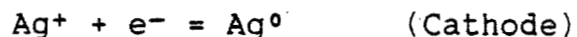
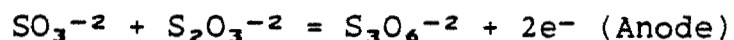
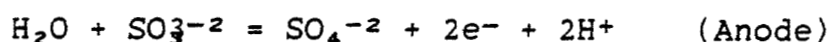
Desilvered fix is not recycled because of the iron contamination. The average iron concentration in the cartridge effluent, over the life of the cartridge, is 4,000 mg/l. However, this is not a problem with bleach-fix which contains iron complexed with EDTA as an active ingredient.



Because of this, metallic replacement silver recovery is a commonly used first step in the regeneration of bleach-fix.

### Electrolytic Recovery

This silver recovery method requires the application of direct current across two electrodes in a silver-bearing solution causing metallic silver to deposit on the cathode. Sulfite and thiosulfate are oxidized at the anode as follows:



Approximately 1 gram of sodium sulfite is oxidized for each gram of silver plated. Considerable agitation and large plating surface areas are necessary to achieve good plating efficiency and high quality silver up to 96-98 percent pure. Lower silver purity levels are usually achieved in tailing cells. The cathodes are removed periodically, and the silver is stripped off. Care must be taken to prevent the current density in the cell from becoming too high to prevent "sulfiding." Sulfiding is the result of decomposition of thiosulfate at the cathode. The sulfide contaminates the deposited silver and reduces recovery efficiency. The higher the silver concentration the higher the current density can be without danger of sulfiding. As the silver is plated out of solution, the current density must be reduced.

Electrolytic units can be used for primary or tailing silver recovery. Primary electrolytic systems are typically installed in two basic ways. One is a batch recovery system where overflow fix from a process line or lines is collected in a tank. When sufficient volume is reached, the waste fix is pumped to an electrolytic cell for the silver removal process. The desilvered fix is either discharged or reused. For reuse, it is pumped to a mix tank where chemicals are added to bring it to replenishment strength. Primary batch system cells are usually designed to desilver the fix at

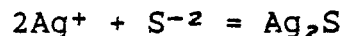
fairly high starting silver concentrations of about 5,000 mg/l. The silver concentration in the effluent is typically about 200-500 mg/l but can be reduced to 20-50 mg/l with additional treatment time and careful control of current density. An electrolytic tailing cell typically achieves the lower range because the process can be optimized for low starting silver concentrations.

The second primary electrolytic recovery method is to remove silver from the fix solution from one or more process machines in a continuously recirculating system at approximately the rate at which silver is being added by processing. The recovery cell is included "in-line" as part of the recirculation system. This continuous removal technique has the particular advantage of maintaining a relatively low silver concentration in the fix processing solution so that the amount of silver carried out with the processed material into the wash tank is minimized. The silver concentration in the fix can be maintained in the range of 500 to 1,000 mg/l, the lower limit being primarily a function of residence time in the cell, i.e., system flow rate.

The recycling of desilvered fix solution, whether by an "in-line" continuous system or by batch, requires adequate monitoring and process quality control to protect product quality. Parameters which should be monitored to maintain the physical and chemical properties of the fix solution include pH, silver, and sulfite concentrations.

#### Chemical Precipitation

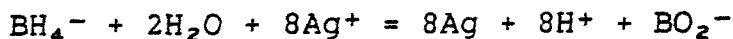
Chemical precipitation is a relatively uncommon method for recovery of silver from photographic processing waste solutions but is practiced widely in the photographic supplies manufacturing point source category. Silver may be precipitated from fixers with sodium sulfide:



The precipitation is quantitative in an alkaline solution, and the resultant silver sulfide has a solubility product of  $10^{-50}$  making it one of the most insoluble substances known.

The physical characteristics are not as favorable as the chemical characteristics. Precipitation must be carried out in alkaline media to avoid the generation of hydrogen sulfide. Silver sulfide tends to form colloidal suspensions. Its very small particle size makes filtration difficult and the filter cake produced is extremely dense. Diatomaceous earth filter aid can be used to improve filtration. About three grams of filter aid are required for each gram of silver, if a conventional filter press is used.

Sodium borohydride is also an effective precipitant for silver:



This precipitating agent can also be used to treat photographic processing wash waters. Sodium sulfide requires very little excess, while borohydride requires significantly more than the stoichiometric reaction quantity to complete the reaction. A major difference between the two precipitating agents is the resulting silver quality. Sodium borohydride produces elemental silver of 90 to 95 percent purity. The sulfide addition generates silver sulfide containing 87 percent silver. Silver concentrations as low as 0.1 mg/l can be achieved by either method.

In a typical system, the precipitating agent is mixed with the silver-bearing waste solution in a batch reaction tank equipped with automatic pH control. The pH is maintained above 7 to avoid releasing toxic hydrogen sulfide gas when sodium sulfide is used.

The optimum pH range for sodium borohydride precipitation is 6.5 to 6.8. The solid particles formed (1-2 microns) are allowed to settle before filtering.

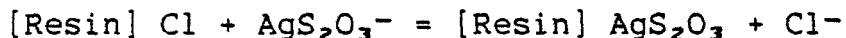
Solutions treated by sodium sulfide or sodium borohydride cannot be reused in the photographic process.

### Silver Recovery from Wash Waters

Even with an efficient fix solution silver recovery system and squeegee use at the exit of the fix tank, up to 10 percent of the available silver is lost to the after-fix wash water by carryover. The silver concentration in the wash water is typically in the range of 1 to 50 mg/l and it has not been found practical to use the previously described conventional silver recovery methods for recovery of this silver. Thus, the concentration of silver is generally too low for effective use of electrolytic or metallic replacement recovery methods. In addition, the iron by-product from metallic replacement precludes the possible wash water reuse without extensive treatment. Although precipitation is technically satisfactory, it is too slow and too expensive because of raw material and filtration costs to be economical.

Two methods have been found to be effective and are currently in use for recovery of silver from wash water, namely resin ion exchange and reverse osmosis (RO). A third method called "low flow prewash" has been used on an experimental basis at two plants. This consists of apportioning the after-fix wash water into two segments, a low volume, high silver concentration prewash and a final wash of low silver content. Silver can be removed from the prewash by conventional methods.

Resin ion exchange is the reversible exchange of ions between a solid resin and a liquid. A variety of weak and strong base anion resins are effective in silver recovery. Using chloride as the mobile ion, the following is representative of the reaction:



The silver complex has a high affinity for the resin and consequently it is difficult to reclaim the silver and regenerate the resin. Recently, a concentrate has been developed that accomplishes this task economically. Other problems such as suspended matter, particularly gelatin, plugging the resin have also been solved by equipment design and operational procedures.

Reverse osmosis is a general separation technique. It involves a wastewater stream flowing under pressure through an appropriate porous membrane. Water passes through the membrane as product and the pollutants remain upstream from the membrane as concentrate. Reverse osmosis is governed by membrane surface phenomena and pore size, as well as wastewater characteristics. The membrane surface must be of such a chemical nature that it has a preferential sorption or repulsion for one of the constituents of the fluid mixture. Consequently, the membrane-liquid interface is enriched in one of the solution constituents. A continuous flow under pressure through the membrane capillaries results in a production solution (permeate) whose composition is different from that of the bulk solution. For recovery of silver from wash water by reverse osmosis, after-fix wash water is equalized, filtered, and then pumped through a reverse osmosis unit. Silver can be removed from the concentrate by conventional silver recovery methods depending on silver concentration and presence of other pollutants. Potential problems encountered with the use of reverse osmosis equipment for recovering silver from wash water are fouling of the membrane and biological growth. Proper maintenance and control are required to alleviate these problems. One plant reported difficulties with membrane fouling which required frequent replacement of the membrane with a resulting high maintenance cost. The problem was alleviated by the use of sand filtration in the waste stream prior to the reverse osmosis unit.

The low flow prewash system is a relatively new concept and is still being evaluated. This system concentrates most of the fix carryout in a low volume after-fix prewash tank. The system consists of segmenting the after-fix wash tank to provide a small prewash section with separate wash water make-up and overflow. The wash water flow can be optimized depending on the carryover silver concentration and the level of treatment. By design, the concentrations of fix, silver, and other chemicals reach high levels in the prewash tank under steady-state conditions. There is concern expressed by some investigators that this may cause problems with the quality of the processed material. In effect, the processed material receives additional fix time and exposure to potential contaminants while immersed in the prewash.

Dye stability tests, performed by one investigator on color paper processed using the prewash system, have shown an increase in yellow stain six months after processing. There is also a requirement for increased maintenance of the wash tank because of biological growth.

#### Coupler Recovery

The three color developers used in the K-14 color reversal process (DC) contain organic dye couplers. Since the couplers are in solution, it is common practice to recover these organic couplers from the waste developer overflow for economic reasons. The couplers are not recoverable from the IC process because they are not in solution. Instead, the color couplers are put into the three emulsion layers during manufacture of the film or paper and remain to form the color image after processing.

The (DC) couplers are soluble in the normally alkaline developers but will precipitate at neutral or acid pH. To recover the couplers, the pH of the waste developer is adjusted to 7 or less with sodium bisulfate and then the precipitated couplers are extracted by centrifugation. Carbon dioxide has also been used for pH adjustment. The photoprocessor may reuse the couplers in the appropriate developer solution. The recovery and reuse of couplers requires proper testing and quality control procedures to avoid problems with color balance and saturation in the processed films.

#### Bleach Regeneration

Bleaches are used in the black and white reversal process to dissolve the negative silver image and in the color process to oxidize the developed silver image to a silver halide which is subsequently dissolved in the fix solution. It is common practice in color processing to regenerate the reduced bleach for reuse by oxidizing the bleach back to its original state or by discharging a portion of the bleach and adding fresh chemicals to restore it to original specifications. The main active ingredient contained in color processing bleaches is either sodium or potassium ferricyanide, ferric EDTA, ferric chloride, or sodium

dichromate. A dichromate bleach is commonly used in black and white reversal processing and is not regenerated. Ferric chloride bleach is also not regenerated. The reuse of regenerated bleaches require various quality control measures, depending on the bleach type and regeneration method, to ensure against adverse effects in the product from improper chemical balance, chemical impurities, and dirt. These problems are addressed in more detail in a preceding subsection on product quality.

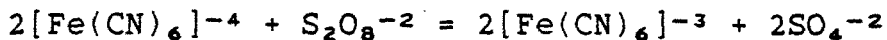
#### Ferricyanide Regeneration

The basis for all the ferricyanide regeneration methods is a sufficiently strong oxidizing agent that has reaction products compatible with or used in the process. Current regeneration processes which fulfill these requirements are:

- A. Persulfate regeneration
- B. Ozone regeneration
- C. Electrolytic bleach regeneration
- D. Miscellaneous chemical regeneration methods

#### Persulfate Regeneration--

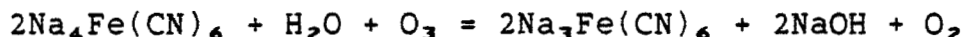
Persulfate regeneration is a batch process consisting of collecting the bleach overflow in a tank and adding potassium persulfate to oxidize the ferrocyanide ion back to ferricyanide by the following reaction:



Bromide is also added to replenish that taken up by the silver during bleaching. One problem with the persulfate method is a build-up of the sulfate ion which slows the bleaching action. To alleviate the problem, about 10 percent of the bleach is directly discharged before regeneration or the bleach drag-out rate in the process tank is regulated by squeegee adjustment so that a comparable sulfate reduction occurs.

### Ozone Regeneration--

The use of ozone for ferricyanide bleach regeneration minimizes the salt build-up problems encountered with persulfate regeneration and reduces the need for bleach blowdown during regeneration cycling. The ozone process is characterized by the following reaction:



Stoichiometrically, 12.7 kg of sodium ferrocyanide are converted to 11.7 kg of sodium ferricyanide using 1.0 kg of ozone. Under varying conditions of pH, the ozone oxidation efficiency is near 100 percent for ferrocyanide concentrations above 1.0 gram per liter.

The pH of the bleach increases as the reaction proceeds, and bromide additions are required to replace the bromide taken up by the silver. Therefore, hydrobromic acid is added to accomplish both pH adjustment and bromide ion addition. Theoretically, one bromide ion is required for each ferrocyanide ion that is oxidized to ferricyanide. The hydrobromic acid avoids all build-up of sulfate and other unwanted by-products. If, in practice, there is a slight build-up of bromide ion, small amounts of sulfuric acid can be added for pH adjustment with little danger of high sulfate build-up.

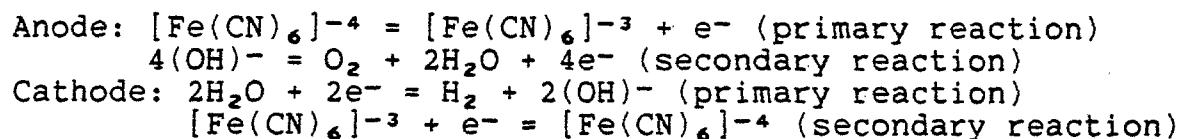
Some photoprocessing plants have installed continuous in-line ozonation for ferricyanide bleach regeneration. This technique permits a significant reduction in the necessary ferricyanide concentration in the bleach tank, since the ferrocyanide level in the solution is kept low and the ferri to ferro ratio is the controlling factor in effective bleaching. With a lower ferricyanide bleach concentration, there is less drag-out and less pollution of the waste wash water.

Ozone can be somewhat hazardous because of its toxicity, but methods have been developed to use it safely. Safe practices include the use of ozone detectors to monitor the air in the vicinity of the ozonation tanks.



### Electrolytic Regeneration--

Ferrocyanide can be oxidized to ferricyanide at the anode of an electrochemical cell. Because the reverse reaction occurs at the cathode, the cell must be divided by a semi-permeable membrane, or some other method of minimizing the cathode reaction must be employed. The electrolytic cell reactions are given below:



With improved cell technology minimizing the undesirable secondary reactions having become available recently, this method of ferricyanide bleach regeneration has found wider acceptance in the photoprocessing industry. Like ozonation, there is no requirement for bleach blowdown during the regeneration cycle.

### Bromine and Peroxide Chemical Regeneration Methods--

Probably the simplest ferricyanide bleach regeneration technique, from a chemical point of view, is the use of bromine. The bromine performs the ideal role of oxidizing the ferrocyanide and replacing the bromide ions removed by the film as it passes through the bleach. It is an economical method, there are no unwanted reaction products, and there is minimal dilution. Because of the hazard and corrosiveness associated with the handling of liquid bromine, however, the method has not been widely accepted.

Bromate and bromite compounds have been used with satisfactory results and are somewhat easier to handle. The main reason for their not being used more widely has been hesitation by the industry to handle chemicals of this nature.

Hydrogen peroxide has also been used successfully. Hydrobromic acid is added to control pH and supply the required bromide ions. However, the problem of handling peroxide has restricted the use of this method.

## Summary of Ferricyanide Bleach Regeneration Methods--

The most popular methods are persulfate and ozone regeneration. Both methods are efficient with the persulfate yielding about 90 percent of the used bleach for recycle and the ozone method allowing 100 percent recycle. Both methods require analytical monitoring of the regeneration process. The persulfate method consists of a single chemical addition requiring no special equipment beyond tanks and plumbing. It does have the problem of sulfate build-up which must be corrected by up to a 10 percent discharge. Ozonation allows essentially 100 percent recycle and is adaptable to continuous in-line regeneration but requires a larger investment in equipment and maintenance. Electrolytic regeneration is a relatively new method but appears to have advantages and disadvantages similar to ozonation.

### Ferric EDTA Regeneration

Modifications in the processing of certain photographic materials have resulted in the substitution of ferric ions chelated with EDTA for ferricyanide as the bleaching agent. The ferric-EDTA bleach relies upon the oxidative power of the ferric ion which is reduced to ferrous ion in the process. Ferric EDTA is used alone as a bleach for certain color films and is used in combination with sodium or ammonium thiosulfate fixer for color paper processing. The combined material is known as bleach-fix.

Regeneration of the bleach involves the oxidation of the ferrous ion back to the ferric ion and the replenishment of various chemicals, principally bromide. Typically the oxidation process is performed as a batch process in a tank with aeration. Some plants aerate the bleach in the process bleach tank using compressed air which serves the dual purpose of solution agitation and oxidation.

Regeneration of the waste bleach-fix solution involves three steps. First, the silver must be recovered. Second, the reduced iron EDTA complex must be oxidized back to ferric EDTA. Finally, certain chemicals lost through carryover

with the film or paper must be added to bring the solution up to replenisher strength.

As with the desilvering of waste fixer solutions, there are several techniques available to remove the silver from bleach-fix waste. The most widely used technique is the silver recovery cartridge containing steel wool where the silver is replaced by iron, and the silver is retained in the cartridge. The metallic replacement method is most widely used both for economic and practical operating considerations. After passing the bleach-fix overflow through the silver recovery cartridge, the resulting solution is aerated to oxidize the ferrous EDTA complex to the ferric form. After aeration, the bleach is returned to a holding tank where make-up chemicals are added as required to restore the solution to replenishment strength.

It is also possible to use electrolysis to recover silver from bleach-fix baths. Equipment has recently appeared on the market which is designed for desilvering bleach-fixers electrolytically. This method has some advantages, such as better control of iron concentration and higher quality recovered silver, over metallic replacement, particularly in larger processing laboratories.

Irrespective of technique, it is possible to reuse between 70 and 80 percent of the bleach-fix by regeneration. The 20 to 30 percent loss is due to a combination of carryout with the paper or film and excess bleach discharged to prevent contaminant build-up.

#### Reconstitution of Dichromate Bleach

Dichromate bleach is found in processes for motion picture color negative print film and in processes for black and white reversal film. The dichromate bleach used in color negative processing has the same function as the ferricyanide and EDTA bleaches, that is, it oxidizes the silver image to silver bromide. However, the function of the dichromate bleach used in black and white processing is to dissolve the silver image. To do this, the bleach formula contains no bromide and is very acidic. As a result the waste bleach contains silver. Before disposal of the

dichromate bleach, silver is usually recovered. This is generally done by adding sodium chloride which precipitates the silver as silver chloride.

A portion of the dichromate color bleach can be reused by discharging approximately 50 percent of the used solution and then adding chemicals to restore its original strength and volume. As discussed in the section on product quality, controls must be used to prevent dirt and unwanted chemical build-up.

Another practice that is used to reduce the waste bleach load is to modify the normal replenishment system to one of "replenishment-by-demand." During the color dichromate bleaching process, the bleach is chemically reduced. The amount of dichromate ion reduction per square foot of film depends on the relative amounts of light and dark areas in the film image. By adding replenishment chemicals "on demand," only the amount of dichromate reduced is replaced, minimizing waste. Demand is determined by monitoring the bromide level. Dichromate ion depletion is proportional to the bromide ion depletion. Normal replenishment rates are based on the maximum potential rate of dichromate depletion per square foot. This practice commonly results in the generation of some excess bleach which must be discharged.

#### Developer Regeneration

Developers become exhausted both by loss of active developing agents and by increase of reaction products. The limiting factor is usually the increased bromide concentration. Two approaches may be taken to reuse developers: (1) the reaction products can be removed by a technique such as ion exchange so that the bulk of the solution may be reused; or (2) specific chemicals can be separated from the bulk of the solution by precipitation or extraction techniques and the treated solution reused with or without further purification. As an example, bromide and developer decomposition products can be removed by ion exchange from color developers; other constituents are not affected. After passing through an ion exchange column, the developer is reconstituted and reused.

Currently, only the ion exchange method is used on a limited basis on some color paper developers. Its applicability to other developers is yet to be determined. Because of the complexity of the developing solution and process, proper control of chemical balance is difficult and may not be possible in some cases.

### Water Conservation

In the photoprocessing industry, the three major areas of plant water use occur in solution preparation, water washing of film and paper, and equipment cleanup. Of these three, the largest single use occurs in film and paper washing. Methods for reduction and conservation of wash water include:

- A. Countercurrent washing
- B. Squeegee use
- C. Automatic wash water controls
- D. Chemical prewash
- E. Water recycle

### Countercurrent Washing

The countercurrent wash system referred to here is the use of a segmented wash tank after one of the process steps, usually the final wash after fix. It does not refer to the practice of pumping the same wash water from one wash tank after a process step to another wash tank after a different chemical processing solution. This practice may interfere with the process chemistry. In the segmented tank system, wash water is cascaded progressively from one tank segment to the next against the movement of the film. Fresh wash water enters the last wash tank segment in the system, and the overflow flows to each preceding segment in succession. As the film or paper moves forward, it progressively comes into contact with cleaner and cleaner wash water. It is reported to be up to a hundred times more efficient than deep-tank washing. The net result is a lower total water input to remove chemical by-products from the film or paper.

Countercurrent washing is not universally applicable to all process machine configurations. When used, proper controls

must be applied to prevent quality problems from biological growth, dirt accumulation, and inadequate washing.

### Squeegees

Squeegees are devices designed to remove the liquid from the surfaces of film and paper as they move from one process tank to another to reduce solution carryover. They are placed at the exit of process solution and wash tanks where such placement is compatible with the process chemicals and emulsion. With proper placement and adjustment, squeegees conserve raw materials and reduce water use and replenishment volume (waste effluent). The amount of carryover reduction varies depending on a number of factors including squeegee type, process material area and machine speed, but typically ranges up to 95 percent. This reduction in carryover can result in a significant reduction of wash water. For example, the recommended wash water rate for the C-41 process without squeegee use is 183 l/sq m and with squeegee use is 91 l/sq m, a reduction of 50 percent.

Squeegee use is not universally applicable to all process machines, chemistry, or products. Proper placement, adjustment, and maintenance are extremely important to prevent physical quality problems from scratches and abrasions.

Among a wide variety of squeegee types, the most common are rubber or polyurethane wiper blades (usually used in pairs with the blades opposed to each other on opposite sides of the film or paper), air knives, Venturi, rotary buffer, and soft rollers. Wiper blades can have rigid mountings or, as more recently used, they are attached to the machine with plastic leaf springs which provide a constant self-adjusting blade pressure on the film. The air knife squeegee consists of slits cut into two opposed tubes from which air impinges on each side of the material at an angle of 20° to 45° off normal. The Venturi squeegee also utilizes air impingement where the material effectively becomes one side of a Venturi orifice. The rotary buffer consists of two opposed soft felt rollers rotating in opposition to the linear motion of the material. Soft rollers are used in opposing pairs. The roller has an inner shaft covered with a soft polyurethane

foam, which in turn is covered with a thin layer of silicone rubber having a very smooth surface. Soft roller squeegees are typically used for wide format materials. In addition to their squeegee action, the rollers aid in transporting the material through the machine and allow self threading which, in turn, means no leader is required.

#### Automatic Wash Water Controls

Excessive wash water flows can be avoided simply and effectively by the installation of automatic solenoid operated shutoff devices which completely stop the flow of water into the processor when it is not being used. A shutoff delay of a few minutes is needed so that time is allowed for removal of excessive chemical by-products carried into the wash water by the film. Further efficiencies can be accomplished by the installation of maximum flow regulation valves which prevent greater flow than needed.

#### Chemical Pre-Wash

After-fix wash water volume can be reduced by 60 to 70 percent with the addition of a salt bath between the fix and final wash. The role of the salt bath is to remove the fix from the emulsion chemically at a faster rate than can be done by washing. The salt bath provides a resultant reduction in washing time and water volume. A satisfactory bath of this type is a 20 grams per liter mixture of sodium sulfate and sodium bisulfite at a pH of 8 to 9.

#### Water Recycle

Wash water recycle has the potential for a significant reduction in a plant's water use. With effective application, along with other in-process controls, total plant process water use has been observed in actual applications to be reduced by about 70 percent. As discussed in the section on product quality, proper quality control is extremely important when recycling wash water. Wash water recycle is not necessarily applicable to all processes or practical in all plants because of product mix. When recycled water is used, the current practice is to

recycle the water to print processes and use fresh water for processing of originals so that in case of control problems irreplaceable originals are not damaged. Methods used for preparation of the water for recycle include treatment with resin ion exchange or reverse osmosis, which were described previously in the section on silver recovery from wash waters.

### Housekeeping

The overall effectiveness of most of the previously discussed in-process controls is greatly reduced if a plant does not have a commitment to good housekeeping practices. The attendant results are a decreased economic benefit and increased pollutant loads.

For example, silver recovery units must be regularly maintained to prevent silver loss. The effluent from metallic replacement units must be carefully monitored and the units replaced when exhausted. The unit is usually considered to be exhausted when the effluent silver concentration is 1,000 mg/l as determined by the use of silver test paper or chemical analysis. Care must be exercised in the operation of electrolytic units to control cell current density to prevent sulfiding, if too high, and the loss of silver, if too low.

Plumbing leaks and the use of excess chemicals and water must be prevented to reduce hydraulic and chemical loads. The replenishment rate used should be the minimum required for proper process operation. The replenishment and wash water control valves should be calibrated and periodically checked for proper flow rate. Automatic control equipment should be used for cut-off of replenishment and wash water at the appropriate time at the start and end of a product run. Squeegees should be used at every solution exit where possible and should be regularly checked for proper squeegee action.

### END-OF-PIPE TREATMENT TECHNOLOGIES

End-of-pipe treatment is the treatment of wastewater from a process just prior to discharge for the purpose of reducing



pollutant loads to the receiving stream. Although benefit may be gained from material recovery, the primary purpose is pollutant reduction. A number of establishments in the photographic processing industry use various types of end-of-pipe treatments.

In many cases the wastewaters are segregated into concentrated chemical wastes and wash water wastes and then treatments are applied to one or both waste streams. The size, complexity, and corresponding costs of the treatment equipment may be reduced by separation of wastewaters.

Descriptions of the end-of-pipe treatment technologies encountered in this industry follow.

Precipitation involves the reaction of two or more soluble chemicals to produce an insoluble product. This technique is used to reduce the amount of iron-cyanide complex being discharged by treating waste fix containing the complex with a flocculant and ferrous sulfate as a reducing agent. This results in the formation of insoluble ferrous ferrocyanide which settles with the aid of the flocculant. Sulfide precipitation is also used in a proprietary process for the reduction of metals such as silver, cadmium, lead, iron, and zinc from photoprocessing wastewater. Because these metals exist as complexes, it is necessary in some cases to break down the complex before effective precipitation can take place. This problem has been overcome by use of proprietary chemical additions.

Precipitation can be used for the reduction of chromium. As used in the electroplating industry, the amount of chromium in the wastewater is reduced by chemical reduction of hexavalent chromium to trivalent chromium and then precipitation of the chromium followed by filtration. The precipitation of chromium involves the addition of caustic soda or lime to the wastewater to increase the pH to 8-10. This decreases the solubility of the chromium, which precipitates as the hydroxide.

Cadmium can be precipitated as the hydroxide by adjustment of pH. Alkalinity has a significant effect on the solubility of cadmium. The theoretical solubility values of

cadmium hydroxide, according to Pourbaix, are approximately the following:

pH	Solubility, mg/l
8	3,000
9	30
10	0.03
11	0.003 (minimum)

The insolubility of cadmium carbonate suggests that precipitations with soda ash may reduce soluble cadmium to very low levels in effluent. Since many combined wastewaters contain some carbonate, it is very possible that cadmium carbonate rather than cadmium hydroxide is precipitated when wastewaters are neutralized with caustic or lime. Some reported values that seem unrealistically low for hydroxide precipitation actually may be achieved by this mechanism.

Cadmium sulfide is very insoluble (solubility product,  $K = 10^{-29}$ ), so that a precipitation system based upon sulfides, combined with efficient removal of dissolved solids, may provide acceptable effluent.

Settling involves the concentration of particulate matter in wastewater by collecting the wastewater in tanks or ponds under quiescent conditions and allowing the suspended matter to settle with time. Waste streams in this industry do not normally contain large amounts of suspended solids; however, settling is commonly used in conjunction with precipitation to remove the resultant solids. Settling was observed to be used for (1) collection of precipitated ferrous ferrocyanide, (2) collection of precipitated metal sulfides, (3) reduction of suspended solids in aerated wastewater, and (4) preliminary settling of wastewater prior to discharge to a POTW.

Ozonation is a treatment process where ozone is bubbled through the wastewater. The wastewater is usually collected in tanks and the ozone added through sparging tubes in the bottom of the tank. Sometimes the wastewater is cascaded through two or more tanks connected in series. The ozone

provides a source of oxygen for oxidizable compounds and is used for the general reduction of BOD and COD in the wastewater. It is also used as a pretreatment for wastewater that is to be further treated by aeration. Plant 7781 has demonstrated that the addition of ozone prior to aeration enhances the effectiveness of the aeration process.

Filtration is used for reduction of waterborne suspended solids. It is accomplished by passing the wastewater stream through solid media such as retaining screens, cloths, or papers or through particulate media such as sand, gravel, carbon, or diatomaceous earth using gravity, pressure, or vacuum as the driving force. The filter equipment includes plate and frame presses, cartridges, and sand or mixed media beds. Filtration is employed to dewater precipitated ferrous ferrocyanide and metal sulfides and as a wastewater preconditioner prior to treatment by ion exchange or reverse osmosis. Diatomaceous earth filtration is used in the electroplating industry for reducing the amount of the previously precipitated chromium hydroxide in the treated wastewater.

Clarification is a unit operation for reduction of suspended solids. A clarifier is a tank with internal baffles, compartments, sweeps, and other directing and segregating mechanisms to separate the solids from the liquids. The solids are contained in the underflow, and the overflow consists of wastewater with reduced solids. Often the underflow, having a high solid content, is sent to a second clarifier or sent directly to a centrifuge or filter device for further concentration to sludge or cake solids. One facility was observed to use the clarifier as both a reaction vessel to precipitate ferrocyanide and as a clarifier to settle the precipitate from the liquid.

Aeration involves the treatment of wastewater with air to cause the reduction of oxygen demand. This is commonly done in ponds or large tanks. The aeration action is enhanced by pumping the wastewater into the air as a fountain or bubbling air through the water by means of sparging tubes in the bottom of the pond. Aeration is used to a limited extent in the Photographic Processing Industry for reduction of BOD and COD.

Neutralization involves the adjustment of the pH of a waste stream with acid or alkali to produce a near neutral condition. The most common method is to treat acidic streams with alkaline materials such as limestone, lime, soda ash, or sodium hydroxide. Alkaline streams are treated with acids such as sulfuric. There is no particular pH control problem in the industry. For example, developer wastes are alkaline and stop and fix wastes are acid. The combined wastes are often nearly neutral. Neutralization is employed at one plant to adjust the pH of wash water treated by reverse osmosis prior to discharge to a POTW.

Equalization involves the collection of wastewater in tanks or ponds for the purpose of equalizing or controlling the flow quantities prior to discharge or other treatment steps. Equalization is necessary and practiced prior to reverse osmosis.

Chlorination involves the addition of chlorine gas or a hypochlorite salt to the wastewater to cause breakdown of certain compounds by oxidation. It is used in the industry to reduce chlorine demand loads in cooperation with the local POTW and for control of slime organisms. It can also be used for odor abatement or as a specific reactant.

Flocculation is used to cause or accelerate the settling and concentration of suspended solids. Solids often settle slowly, or not at all, because of small size and electrical charge. Addition of flocculants such as alum, ferric chloride, and polymeric electrolytes promotes coagulation of particles and gives faster settling rates and improved separation. This process is used as an aid in the settling of precipitated iron-cyanide complexes.

Reverse Osmosis is a physical separation technique that involves a wastewater stream passing under pressure through a membrane. Water passes through the membrane as product (permeate) and the pollutants remain upstream from the membrane as concentrate. Reverse osmosis is used in the industry to reduce pollutants in the relatively dilute wash water wastes. This reduction of pollutants allows the recycle of the permeate and is practiced at several plants.

Evaporation is a technique that is used to reduce the volume of a wastewater stream. The one plant using this system recycled most of the processing chemicals and wash water to reduce the hydraulic load input to the evaporation system. The evaporation system consists of two stages of evaporation in a spray film evaporator with a third and final evaporation stage in a hot oil wiper film evaporator. Thermal energy is conserved by pre-heating the incoming water by directing it through the condensation tubes in the first evaporator and by storage of the wastewater between stages in thermally insulated tanks. The solids content of the wastewater is concentrated from 2 to 65 percent in the first two evaporation stages. The sludge remaining after the third stage of evaporation is about 85 percent solids. The evaporated water is condensed, purified, and reused in the process as wash water. The purification process, consisting of ion exchange, is necessary to remove ammonia compounds.

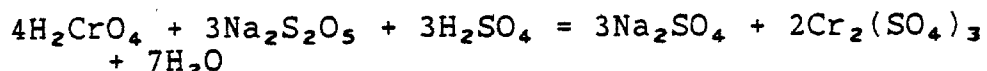
Chemical Reduction of Hexavalent Chromium - Chemical reduction is used for the treatment of wastewater by the electroplating industry for the reduction of hexavalent chromium to trivalent chromium. The reduction enables the trivalent chromium to be separated from solution by alkaline precipitation followed by diatomaceous earth filtration.

Reduction is a chemical reaction in which one or more electrons are transferred to the chemical being reduced from the reducing agent. Hexavalent chromium (CrVI) is usually reduced to trivalent chromium at a pH of 2 to 3 with sulfur dioxide (SO<sub>2</sub>), sodium bisulfite, other sulfite-containing compounds, or ferrous sulfate. The reduction makes possible the removal of chromium as the trivalent hydroxide which precipitates under alkaline conditions. Typical reactions for SO<sub>2</sub> reduction are:

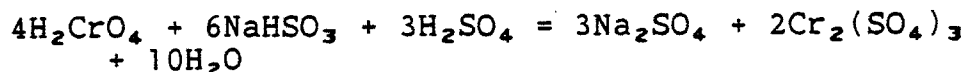


Representative reactions for reduction of hexavalent chromium under acid conditions using sulfite chemicals instead of SO<sub>2</sub> are:

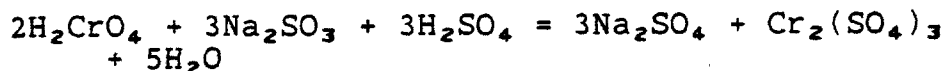
(a) sodium metabisulfite with sulfuric acid:



(b) sodium bisulfite with sulfuric acid:

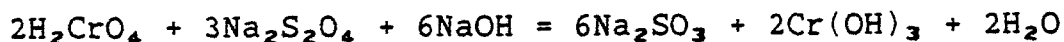


(c) sodium sulfite with sulfuric acid:



Reduction using sulfur dioxide is the most widely used method in the metal finishing segment of the electroplating industry, especially with larger installations. The overall reduction is readily controlled by automatic pH and oxidation-reduction potential instruments. Treatment can be carried out on either a continuous or batch basis.

Hexavalent chromium is also reduced to trivalent chromium in an alkaline environment using sodium hydrosulfite as follows:



Data from the specific plants employing these technologies are presented in Section V and their effectiveness is discussed in Section VII.

#### INDUSTRY CHARACTERISTICS

Information on the general characteristics of plants in the photographic processing industry has been collected in two industry surveys. The first, performed by the Eastman Kodak Company during the period 1969 through 1974, contains information on 237 plants. The results of this survey are summarized in Table III-4. Within a given category, e.g., method of waste disposal, the parts may add up to more than 100 percent. This is because in many cases more than one method of disposal may be used in a given plant. The totals

for each category do not necessarily equal 237 because some plants were unresponsive for some categories. The information included in this survey was collected from plants which had requested information from Kodak on waste disposal or effluent calculations. It is recognized that the information included in Table III-4 is six to eleven years old. Many of the processes in use at that time are obsolete, and it is likely that many of the individual plant characteristics have changed over this time period. Nevertheless, the data were valid at the time of the survey and can serve as a reference point for comparison with the more current information which follows.

A more recent survey conducted by EPA in the spring of 1977 is summarized in the following tables. Table III-5 correlates production and water use with the plant type, arranged by SIC code. SIC codes were not directly addressed in the telephone survey, rather the plant representative was asked what kind of customer the plant served. This information was used to place the plant in a SIC code using best available judgment. Tables III-6 to III-15 correlate various plant characteristics with production categories.

The 139 plants in this survey were contacted by telephone and asked questions according to a fixed format. The answers were recorded on a Telephone Survey Form, a blank sample copy of which is included in Appendix A. Prior to contacting the plant, a letter was sent to the plant explaining the purposes of the EPA program, and giving notification that they would be called and the type of information that would be requested. The list of plants contacted was compiled from trade magazine advertisements, membership directory of the Photographic Marketing Association (PMA), information supplied by the National Association of Photographic Manufacturers (NAPM), previous surveys, and personal contacts. The methods used to obtain plant lists tended to bias the selected plant sample towards relatively large plants [production greater than 93 sq m (1,000 sq ft) per day]. The information available at the time on the identity of the almost 10,000 smaller plants was insufficient for the selection of a random sample of the entire industry.

TABLE III-4

## SUMMARY OF KODAK "200" PLANT SURVEY

METHOD OF WASTE DISPOSAL *	TOTAL (237) *	Distribution of Plants by Water Use					
		up to 1,000 gal/ day (27)	1,000-10,000 gal/day (92)	10,000-50,000 gal/day (64)	50,000 gal/day (28)	over 50,000 gal/day (26)	
		(25)	(83)	(60)	(28)	(15)	
<u>METHOD OF WASTE DISPOSAL</u>	(212) *						
Direct Discharge	6.1%	4 %	6 %	10 %	3.5%	0 %	
Municipal Sewer	83.5%	88 %	89 %	73.5%	96.5%	80 %	
Pretreatment Prior to Municipal Sewer	8 %	0 %	7.2%	6.7%	25 %	0 %	
On-Site Treatment	9 %	8 %	7.2%	21.7%	3.5%	20 %	
<u>SILVER RECOVERY</u>	(191)	(22)	(78)	(55)	(27)	(9)	
Metallic Replacement	66 %	50 %	75.7%	65.5%	66.7%	22 %	
Electrolytic	36 %	9.1%	23.1%	49.1%	74 %	22 %	
Other	5.2%	4.5%	3.4%	7.3%	3.7%	11 %	
None	5.8%	41 %	7.7%	0 %	0 %	45 %	
<u>BLEACH REGENERATION</u>	(179)	(5)	(79)	(54)	(27)	(7)	
Persulfate	55.8%	20 %	49.3%	74.2%	70 %	14.3%	
Ozone	1.7%	0 %	0 %	0 %	7.5%	14.3%	
Aeration	4.5%	40 %	2.6%	5.4%	0 %	14.3%	
None	42.5%	40 %	50.7%	25.8%	22.5%	71.4%	
<u>BLEACH-FIXER</u>	(72)	(4)	(35)	(22)	(9)	(2)	
Regeneration	85 %	50 %	80 %	95.5%	100 %	50 %	
No Regeneration	15 %	50 %	20 %	4.5%	0 %	50 %	

\*Number of Photographic Processing Plants is Indicated in Parentheses

Data compiled during period 1969-1974.

III-64  
88



III-65  
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TABLE III-4 (continued)

		Distribution of Plants by Water Use					
		TOTAL (237) *	up to 1,000 gal/ day (27)	1,000-10,000 gal/day (92)	10,000-50,000 gal/day (64)	over 50,000 gal/day (28)	Unknown gal/day (26)
REUSE OF OTHER SOLUTIONS	Yes	(192)	(20)	(78)	(54)	(28)	(12)
	No	16.7% 83.3%	0 % 100 %	5.1% 94.9%	18.5% 81.5%	64 % 36 %	0 % 100 %
REUSE OF WASH WATERS	Yes	(176)	(22)	(79)	(46)	(23)	(6)
	No	5.7% 94.3%	5 % 95 %	2.5% 97.5%	13 % 87 %	13 % 87 %	0 % 100 %
USE OF SQUEEGERS	Yes	(84)	(8)	(37)	(28)	(14)	(1)
	No	63.2% 36.8%	37.5% 62.5%	65 % 35 %	64.3% 35.7%	86 % 14 %	0 % 100 %
WASH WATER CONTROLS	Yes	(107)	(15)	(49)	(27)	(13)	(3)
	No	41 % 59 %	40 % 60 %	27 % 63 %	44.5% 55.5%	61.5% 38.5%	0 % 100 %
ROD <sub>5</sub> LOADING (lbs/day)	10	(227)	(26)	(90)	(62)	(27)	(22)
	10-100	22.5%	88.5%	16.6%	1.6%	0 %	54.6%
	100-500	48.9%	11.5%	79 %	45.2%	3.7%	36.4%
	500	21.1%	0 %	4.4%	43.5%	59.3%	4.5%
		7.5	0 %	0 %	9.7%	37 %	4.5%

\*Number of Photographic Processing Plants is Indicated in Parentheses

TABLE III-5

CORRELATION OF TYPE OF SERVICE WITH PRODUCTION AND WATER USE  
FROM TELEPHONE SURVEY INFORMATION

Type of Service	Production*					Water Use**					Total
	1	2	3	4	5	1	2	3	4	5	
SIC 7221 Portrait Studio	1	1	2	1	0	5	0	3	2	0	5
SIC 7333 Commercial	8	2	8	2	2	22	6	5	8	3	22
Industrial (X-ray, Aerial)	10	1	3	0	0	14	8	2	2	0	14
Publishing	0	0	0	1	1	2	0	0	1	0	2
SIC 7395 Amateur	10	6	47	9	9	81	7	15	48	9	81
Professional	11	3	15	3	3	35	4	12	15	2	35
Military	2	0	0	0	0	2	2	0	0	0	2
Government	1	3	1	0	0	5	1	3	1	0	5
SIC 7819 Movie, TV	0	2	2	4	0	8	0	1	2	4	8
Unknown	1	0	0	1	0	2	0	1	0	0	2
Totals	44	18	78	21	15	176***	28	42	79	18	176***

## \* Production key

- 1 = less than 1,000 sq ft per day  
 2 = 1,000 to 2,999 sq ft per day  
 3 = 3,000 to 20,000 sq ft per day  
 4 = greater than 20,000 sq ft per day  
 5 = unknown

## \*\* Water Use key

- 1 = less than 1,000 GPD  
 2 = 1,000 to 9,999 GPD  
 3 = 10,000 to 100,000 GPD  
 4 = greater than 100,000 GPD  
 5 = unknown

\*\*\* Total number of plants greater than 139 caused by double accounting, i.e., a plant fits into more than one category.